Selective recovery of metal salts from aqueous streams using ionic liquids

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Selective recovery of metal salts from aqueous streams using ionic liquids

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
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in het openbaar te verdedigen op
maandag 9 november 2015 om 16:00 uur

door

Dries Gerard Cecile Parmentier

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Knowledge is valuable

and the knowledge you gained cannot be stolen from you

from my grand-mother Agnes Viaene

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Table of content

Chapter 1: Introduction

Chapter 2: Selecting a suitable ionic liquid

Chapter 3: Mechanism of metal extraction

Chapter 4: Changing the selectivity due to pH and chloride concentration

Chapter 5: Regeneration of the ionic liquid

Chapter 6: Continuous process for selective metal extraction

Chapter 7: Combine electrospray with ionic liquids

Chapter 8: Ionic liquids as concentrate phase in the electrodialysis process

Chapter 9: Selective sodium extraction with ionic liquids

Chapter 10: Techno-economical evaluation of metal extraction with ionic liquids

Chapter 11: Conclusion and outlook

Chapter 1

Introduction

1.1. No life without water

On November 26, 2011, the month when I started my PhD thesis at Wetsus, NASA launched from Cape Canaveral *Curiosity,* a car-sized robotic rover that has to explore the Gale Crater on Mars. One of the rover's goals was to investigate if the crater ever offered environmental conditions favorable for microbial life and to study the role of water in this.[1,2] For centuries, there is a lot of research going on to find extraterrestrial liquid water, i.e. water in its liquid state that is found beyond Earth. Reason is that it is generally believed that water on earth and in the universe is a necessary condition for life, next to essential chemical elements for biological processes and sources of energy that can be applied by living organisms. Water is of utmost importance for life, because it is a polar molecule and a solvent, which plays a key factor for most of the chemical reactions critical for life.[3]

The Earth is sometimes referred to as the oceans planet and is seen as a majestic blue marble, especially by the privileged few who have gazed upon it from outside earths stratosphere. This is due to the prevalence of water on the planet’s surface. Earth’s surface-land-to-water ratio is 29% land to 71% water. The total amount of water on earth, consisting out of the free water in liquid, solid, or gaseous states in the atmosphere, on the earth’s surface, and in the crust down to the depth of 2000 meters is huge. However, 97.5 percent of this amount is saline water, and only 2.5 percent is fresh water, see Figure 1.1. The greatest portion of fresh water (68.7 percent) is in the form of ice and permanent snow that is covering the Antarctic, the Arctic, and the mountainous regions. Fresh groundwater comprises 29.9 percent of fresh water resources. Only 0.26 percent of the total amount of fresh water on the earth is concentrated in lakes, reservoirs, and river systems. The latter water sources are very important for water ecosystems and most of life on earth.[4]

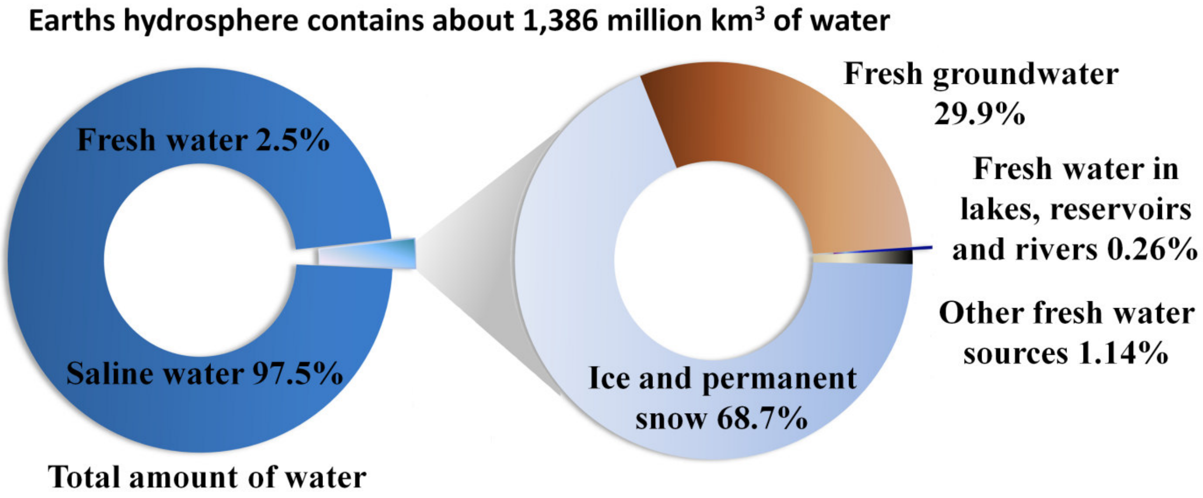


***Figure 1.1**. Distribution of water on earth.*[4] *Other fresh water sources stand mainly for ground ice and permafrost, but also for the water present in soil moisture, in swamps and marshes, in living organism and in the atmosphere.*

With intensified land use, deforestation, climate change and an increased consumption of fresh water by a growing population and industry, it is understandable that fresh water resources are under pressure. Next to this, fresh water is also unequally distributed over the earth, which leads to more and more conflicts around the world. Additionally, also the quality of this water is threatened by an increasing pollution due to urbanization as well as to agricultural and industrial activities. In 2007, the United Nations Department of Economic and Social affairs estimated that around 1.2 billion people, or almost one-fifth of the world's population, live in areas of physical water scarcity, and 500 million people are approaching this situation (water scarcity is when a country or region has an annual water supplies that drops below 1,000 cubic meters per person per year).[5,6] Another 1.6 billion people, or almost one quarter of the world's population, face economic water shortage (where countries lack the necessary infrastructure to take water from rivers and aquifers). They also estimated that by 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity, and two-thirds of the world population could be under water stress conditions (water stress is when a country or region has an annual water supplies that drops below 1,700 cubic meters per person per year).[5]

A process that is often applied by countries to overcome this shortage of fresh water is sea water desalination. This process removes salt from the virtually unlimited supply of seawater, and has emerged as an important source of fresh water. In 2016, the global water production by desalination is projected to exceed 38 billion m^3 per year, twice the rate of global water production by desalination in 2008.[7]

1.2. Metal resource recovery

Next to water, also metals are necessary and valuable for industrial purposes and are applied in consumer goods, e.g. car, computer, cellphone. Therefore, countries around the globe want to secure reliable, sustainable and undistorted access of certain metal ores. However, these ores are also not evenly distributed around the world and getting access to them is a growing concern. Recently, in 2014 the European Commission made a report in which they identified 14 metals and minerals with a high industrial demand, but limited production sources.[8] To overcome this problem, research is focusing on the recovery of valuable metals out of end-of-life products and other waste streams.[9] One important waste stream is waste water. In the past, metal polluted waste water streams were connected to industrial sources. In recent years, metal production emissions have decreased in many countries due to legislation, improved cleaning technology and altered industrial activities. Today and in the future, dissipated losses from consumption of various metal containing consumer goods are of most concern.[10,11]

1.3. Current desalination technologies

Desalination of sea (or saline) water has been commercially practiced for over 50 years. First, desalination was done by distillation, but in the 1970s a switch was made towards commercial membrane processes, such as reverse osmosis (RO). These two main directions survived the crucial evolution of desalination technology, namely evaporation and membrane techniques.[12]

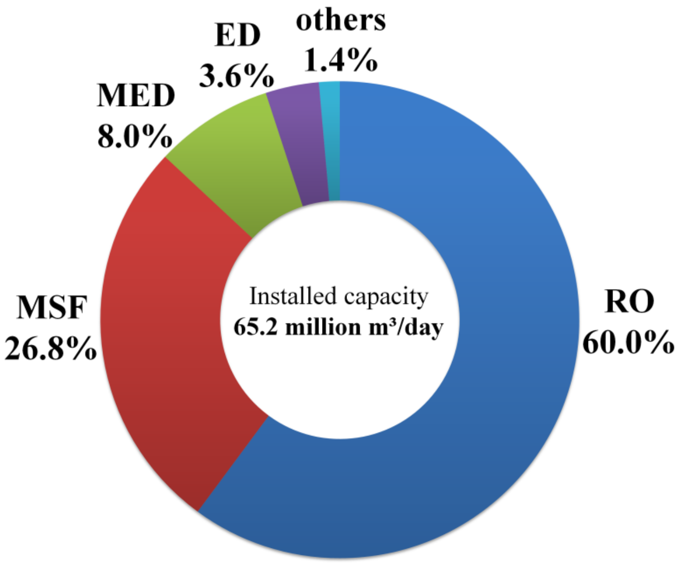


Figure 1.2. *Global desalination capacity (volume) by process in 2010. RO: Reverse osmosis; MSF: Multi-stage flash distillation; MED: Multiple-effect distillation; ED: Electrodialysis; Other: includes; electrodeionisation, eutectic freeze crystallization, nanofiltration, thermal and all other processes.*[13]

1.3.1. Desalination technologies based on evaporation and distillation.

One of the desalination processes that is based on evaporation, called multi-stage flash (MSF) distillation, is until today a common technique for desalination mostly found in the Persian Gulf.[14] The MSF distillation process is based on the principle of flash evaporation. This means, that the seawater is evaporated by reducing the partial water pressure as opposed to raising the temperature. Generally, only a small part of the water flashes to steam, as the phase transition from liquid to gas cools down the remaining liquid. However, when the pressure is decreased even further, the remaining water will start boiling again. Afterwards, the produced steam passes along heat-exchangers, where it is condensed and collected as fresh water. The efficiency of the MSF technology is achieved by regenerative heating from which the flashing seawater in each flash chamber or stage gives up some of its heat to the seawater going through the flashing process stages, see Figure 1.3. The heat of condensation released by the condensing water vapour at each stage gradually raises the temperature of the incoming seawater. Success of MSF is mainly due to its simple layout, easy to operate and maintain, and reliable performance over the years.

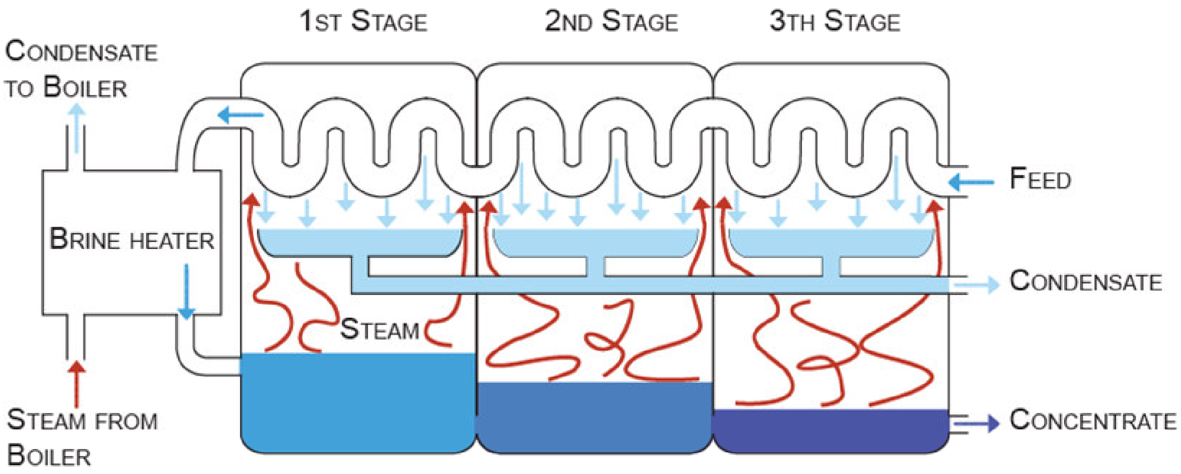


Figure 1.3. *Schematic overview of the multi-stage flash process.*[15]

Among other evaporation techniques, the multi-effect distillation (MED) should also be mentioned here. This is the oldest desalination method and is thermodynamically very efficient.[16] The MED process takes place in a series of evaporators called effects, and applies the principle of reducing the ambient pressure in the various effects, see Figure 1.4. This process permits the seawater feed to undergo multiple boiling steps without supplying any additional heat after the first effect. The seawater enters the first effect and is raised to its boiling point while being sprayed on the surface of evaporator tubes to promote rapid evaporation. These tubes are in the first effect heated by externally supplied steam from a normally dual purpose power plant. The generated water vapor is then applied in the evaporator tubes of another effect to evaporate incoming seawater. By doing this, it condenses in these tubes to obtain fresh water, and the generated water vapor is then applied to heat up fresh seawater in a next effect. Although, both the MSF process and the MED process consume a larger amount of energy compared to membrane process, about 18 kWh/m^3 for MSF, 15 kWh/m^3 for MED, and 5 kWh/m^3 for reverse osmosis (RO), they are still competitive compared to RO due to their reliable performance.[17]

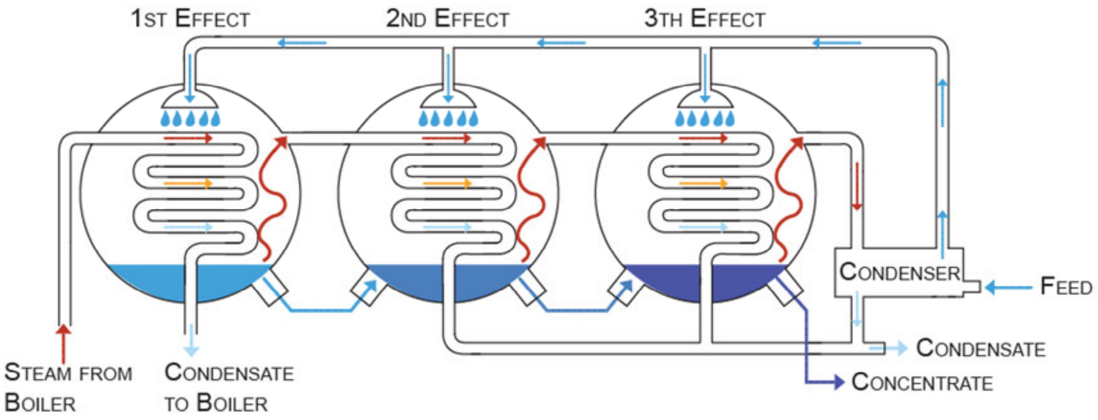


Figure 1.4. *Schematic overview of multi-effect distillation.*[15]

1.3.2. Membrane-based desalination technologies

The reverse osmosis (RO) membrane technique is at this moment the most applied technique for brackish and seawater desalination.[12,18] The RO uses a dynamic pressure (for Seawater RO on average 5500–8000 kPa)[18] to overcome the osmotic pressure of the treated salt solution, resulting in the water-selective permeation from the saline side of a membrane to the freshwater side (see Figure 1.5).[19] Salts, colloids and other charged particles are not permeable through the membrane, and hence, the separation is accomplished. RO membranes are constantly under influence of scaling and fouling. Therefore, careful pre-treatment is needed in order to prevent membrane contamination and fouling. Additionally, also anti-scalents are added in order to prevent precipitation of the dissolved salts due to an increased concentration. Direct sea discharge of the remaining brine solution and the anti-scalents are now causing huge environmental concerns.[20]

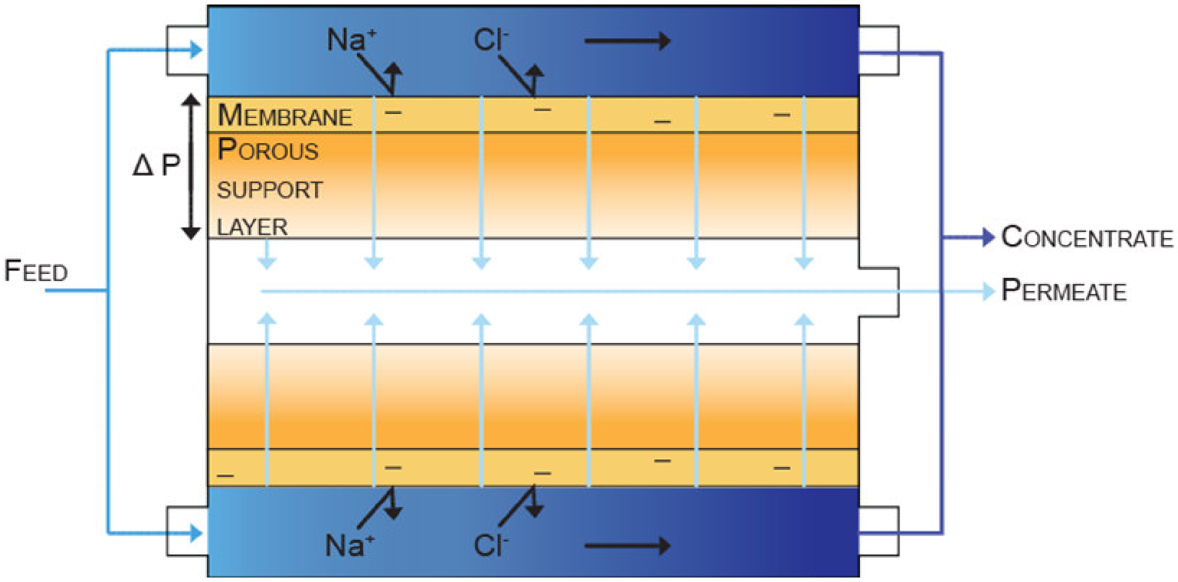


***Figure 1.5**. Schematic overview of the reverse osmosis process.*[15]

Electrodialysis (ED) is another membrane separation technique that mainly focuses on the application of brackish water desalination and treating industrial process water.[21] In this technique, which is shown in Figure 1.6, cation exchange membranes (CEMs) are arranged alternated with anion exchange membranes (AEMs), while a direct current (or voltage) is applied.[22,23] As a result of the potential difference between the electrodes, the cations migrate towards the negatively charged electrode, while the anions migrate in the direction of the positively charged electrode.[24] Positively charged ions permeate through the negatively charged CEM and are blocked by the AEM, whereas, negatively charged ions permeate through the positively charged AEM and are blocked by the CEM.[25] This results in the separation of the ions towards a dilute stream and an ion concentrated stream (concentrate).

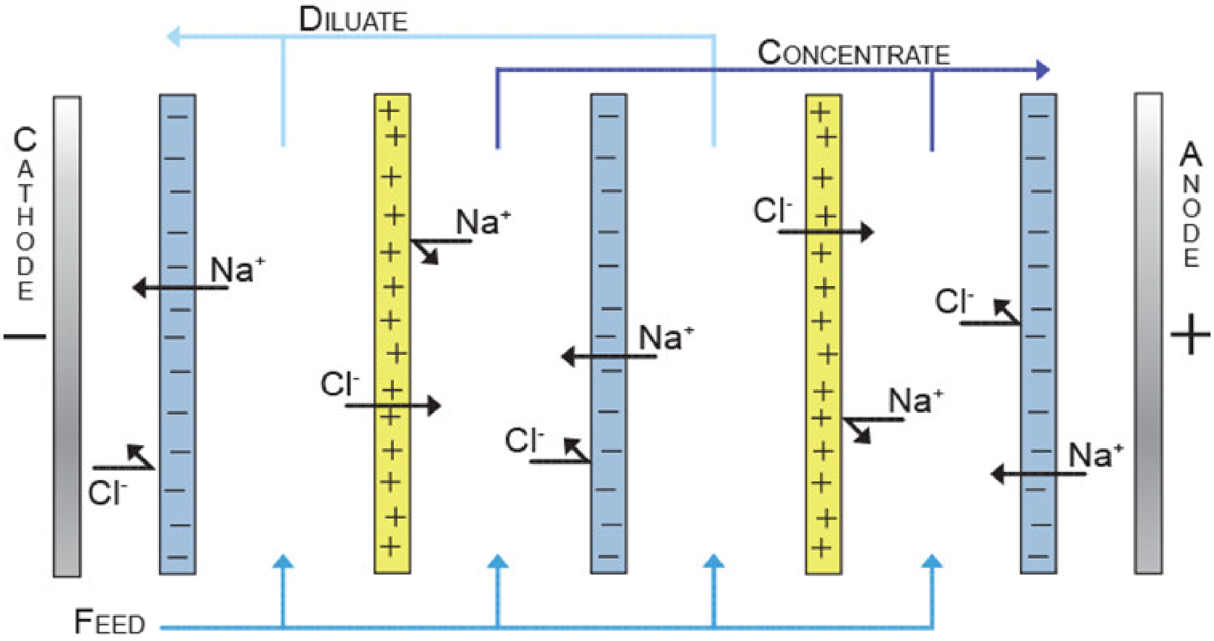


Figure 1.6. Schematic overview of the electrodialysis stack by which diluted and concentrated streams are formed.[15]

1.4. Limitations of current desalination methods

Nowadays, desalinations are well-established processes that are able to produce large quantities of fresh water of excellent quality. Challenges, however, still exist to produce desalinated water for relatively large communities, for their continuous growth, development, and health, and for modern efficient agriculture, at affordable costs. Main problem for these processes is still their high energy consumption. Reason is that current desalination technologies remove the majority compound (water) from the saline solution. Seawater namely exist approximately 96.5% out of water and 3.5 % salt. From an energetic point of view, it would instead be more efficient if there would be a desalination technique that could selectively remove the minority compound (salt) from the saline water.

Ion-exchange resins are well-known to remove salts from an aqueous stream. They are, generally spoken, functionalized copolymers of styrene and divinylbenzene, with a high internal surface area that absorb ions based on the principle of ion-exchange (see Figure 1.7.). Proton or sodium ions from the resins are normally exchanged for other metal cations from the aqueous phase in cation exchange resins while hydroxide or chloride ions in anion exchange resins are normally exchanged for other anions from the aqueous phase. Packing these resins into columns results in a process with high removal efficiencies, high exchange rates, and selective removal of dissolved metals cations or anions.[26] However, because the mechanism is based on ion exchange, the process results in the enrichment of proton, sodium, hydroxide or chloride ions in the treated water phases depending on which type of ion-exchange resin was applied. In the case of proton or hydroxide ions this will then result in a change of the pH for the treated water. Additionally, these resins also need to be regenerated at fixed intervals using strong acids or bases, and recovery of the removed metals for its posterior use is made more difficult.[27] Therefore, desalination of seawater (on average 35 g/L salts) or other highly concentrated salt streams with ion-exchange resins is not economically feasible.

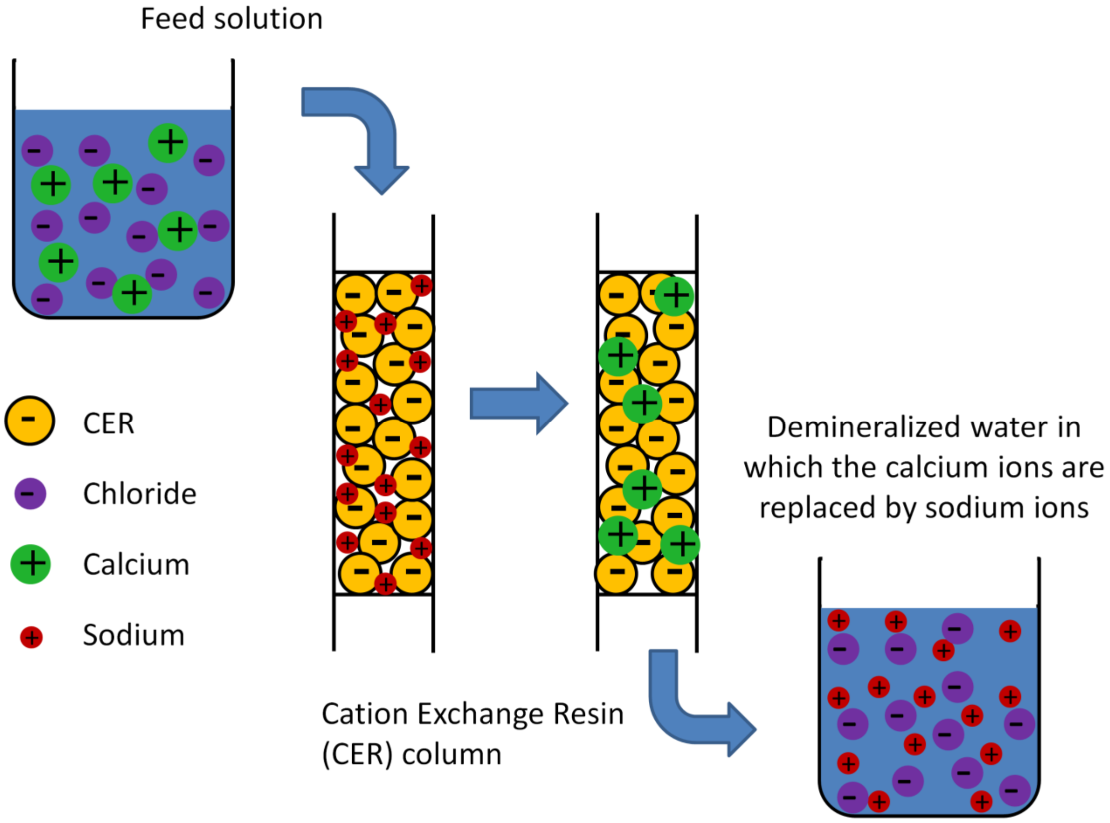


Figure 1.7. *Principle of a cation exchange resin (CER) for the demineralisation of a calcium rich feed stream.*

1.5. Ionic liquids based desalination technology

All previously discussed desalination techniques are already well established techniques and the prognosis is that they cannot be significantly improved anymore.

Therefore, the general idea is that to obtain better desalination techniques in terms of energy consumption, one has to think completely out of the box. One of the novel ideas to develop an improved desalination technique is based on applying ionic liquids as selective salt extractants.

It is generally believed that the study on ionic liquids (ILs) started in 1914 with a report by Paul Walden. He investigated the properties of ethylammonium nitrate, $[EtNH_3^+][NO_3^-]$, and discovered that this anhydrous salt has a melting temperature below room temperature.[28,29] Although at that time, IL research did not attract the interest of scientists, today ILs are examined and implemented in various industrial fields. While ordinary salts melt at very high temperatures, ILs, which are the composite of organic cations and diverse anions, stay liquid at room temperature or at least below 100 °C. Compared to conventional solvents, the unique properties of ILs (see below) and the possibility to tune their properties by changing the cation-anion combination, favours their application in many processes. Therefore, they are considered as designer solvents. Common cations and anions forming ILs and their abbreviations are presented in Figure 1.8. Here is a brief overview of their properties:

Melting point

ILs are so different from other conventional salts, because most of them have a melting temperature around room temperature. This is the result of their composition based on big organic ions, which do not fit nicely into a crystal lattice. In general, it is believed that the size and asymmetry of the ions in the IL are recognized as the important factors that influence the packing of these ions and hereby influence their melting points. Other factors that have an influence are the charge distribution on the ions, H-bonding ability, π-π interactions, dipolar interactions and Van der Waals interactions.[30]

Volatility

ILs have a negligible vapour pressure due to the strong Coulomb attractions between the ions in the IL. Therefore, they are often called “green solvents” because their low volatility prevents pollution of the air and avoids toxic contact by inhalation compared to conventional organic solvents. Their negligible vapour pressure also makes them less flammable. However, high temperatures can result in flammable decomposition products.[31]

Thermal and chemical stability

The liquid range of ILs is often much broader than for conventional solvents. At increased temperature molecular solvents start to boil, whereas ILs mostly decompose before the boiling point is reached. Decomposition temperature depends on the structure of the cation and anion.[32,33] Selecting chemical stabile ions to compose the IL also results in ILs with excellent chemical stabilities.[34]

Toxicity and biodegradability

The reputation of ILs as "green solvents" is based primarily on their negligible vapor pressure. Nonetheless, the solubility of common ILs in water and their toxicity to aquatic organisms is concerning. It is generally accepted that incorporation of aromatic rings in the cations or applying perfluorinated anions results in ILs with an increased toxicity towards organisms. Introducing functional polar groups to the alkyl chain of the ions can reduce the toxicity of ILs and increase the biodegradation efficiency to some extent. On the other hand, increasing the alkyl chain length of the cation, or lipophilicity, results into an increased rate of degradation, but also in an increase in toxicity.[35,36] All this indicates that conscious design of ILs is necessary to deliver truly biocompatible ILs without adversely affecting their properties and performance.[37]

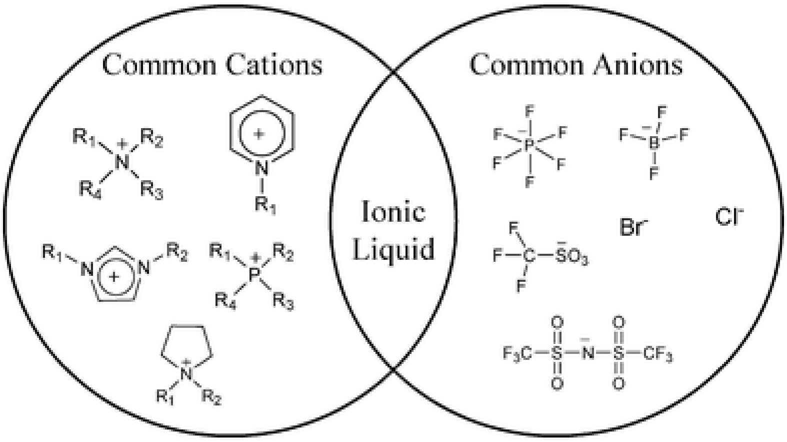


Figure 1.8. *Common structure of ionic liquids.*[38] *For the common cations we observe from left to right, top to bottom: tetraalkylammonium, N-alkylpyridinium, 1,3-dialkyimidazolium, tetraalkylphosphonium and N,N-dialkylpyrrolidinium. The circle of the common anions presents from left to right, top to bottom: hexafluorophosphate, tetrafluoroborate, trifluoromethanesulfonate, bromide, chloride and bis(trifluoromethanesulfonyl)imide*

Due to their interesting properties, ILs have a large potential for a wide variety of applications in industry. Well established applications are e.g. gas separation[39,40] and purification,[41] electrolytes for batteries,[42] dissolution of cellulose[43] or dissolving metal oxides.[44,45] In the last two decades, ILs have also been applied as replacement for conventional solvents in solvent extraction systems. This is not only due to their special properties such as their low flammability, low volatility and broad liquid range, but also because of their specific structure and coordination ability.[46,47] ILs exist entirely out of ions, which makes them very good in stabilizing other ionic species, such as metal ions dissolved in the water phase.

In previous studies, metal extraction by applying ILs were mostly done by dissolving metal extractants into the ILs. Selecting a specific IL and metal extractant resulted in excellent metal extraction efficiencies. However, these solvent extraction systems were based on ion-exchange,[48] resulting in an increasing dissolution of the IL into the aqueous phase, which cannot be regarded as durable and environmentally friendly.[49] To overcome this problem of ion-exchange, hydrophobic ILs were developed with metal interacting functionalities incorporated into their structure.[50] Selecting specific metal interacting functionalities results then in ILs that are selective towards one specific metal or a group of metals. **Aim** of the work reported in this thesis was to investigate if it is technically and economically feasible to apply ILs for desalination. First, good IL candidates for metal extraction had to be selected from literature followed by a thorough investigation of their mechanism. Afterwards, a hydrophobic IL had to be developed, without using toxic ions, that is able to selectively extract metal salts based on the principle of ion-pair extraction. The selected IL would then be applied in a continuously operated metal extraction setup and based on the obtained results a comparison has to be made with existing desalination technologies.

1.6. Scope of this thesis

Chapter 2 describes the development of a novel hydrophobic fatty acid based IL that is capable of extracting heavy metals, while minimizing the risk of polluting the treated water phase with organic ions.

The mechanism of metal extraction for the transition metal ions nickel, cobalt and zinc is reported in detail in **chapter 3**. It was found that the mechanism for nickel and cobalt is different from the metal extraction mechanism for zinc.

The gained knowledge of the extraction mechanism resulted into the insight that the extraction mechanism is pH and chloride concentration dependent for light metals, transition metals and rare earth metals. Furthermore, **chapter 4** also discusses the remarkable low viscosity of this bulky and long-chained IL due to the uptake of water.

Chapter 5 reports investigations on the chemical regeneration and electrodeposition of the metals in the loaded IL. A sodium oxalate solution was demonstrated to be a good way to strip the IL without preventing its reuse.

A continuous metal extraction setup was developed and described in **chapter 6,** in which cobalt was selectively extracted from an aqueous solution containing also the chloride salts of potassium and calcium. Furthermore, an economical study of this process and a toxicological study on the fatty acid based IL was performed.

The next two chapters described the results of two possible ways to improve the metal extraction process with ILs. **Chapter 7** reports the results of the investigation to combine ILs with electrospray to enhance the rates of metal extraction. Implementing ILs into the electrodialysis process to overcome water transport and to avoid polluting the water phase with organics from the IL was reported in **chapter 8**.

Previous chapters mainly focus on the selective extraction of the transition metals (nickel, cobalt or zinc). Instead, in **chapter 9** the synthesis of a sodium selective organic crystal based on the monensin anion is described.

In **Chapter 10** a techno-economical feasibility study is given of the continuous metal extraction setup based on ILs and other desalination techniques based on ILs are also discussed.

Chapter 11 describes the conclusions of the research chapters in this thesis, including an outlook of the implementation of ionic liquids as a novel desalination technique.

1.7. References

1 J. P. Grotzinger, J. Crisp, A. R. Vasavada, R. C. Anderson, C. J. Baker, R. Barry, D. F. Blake, P. Conrad, K. S. Edgett, B. Ferdowski, R. Gellert, J. B. Gilbert, M. Golombek, J. Gómez-Elvira, D. M. Hassler, L. Jandura, M. Litvak, P. Mahaffy, J. Maki, M. Meyer, M. C. Malin, I. Mitrofanov, J. J. Simmonds, D. Vaniman, R. V. Welch and R. C. Wiens, *Space Sci. Rev.*, 2012, **170**, 5–56.

2 D. Preston and C. Felcia, *The Solar System and Beyond is Awash in Water*, 2015.

3 M. Abu-Zeid, *Water Policy*, 1998, **1**, 9–19.

4 I. A. Shiklomanov, *Water Int.*, 2000, **25**, 11–32.

5 UN, *coping with water scarcity - challenge of the twenty-first century*, 2007.

6 M. Falkenmark and G. Lindh, *Water for a starving world*, Westview Press, 1976.

7 Q. Schiermeier, *Nature*, 2008, **452**, 260–1.

8 European Commision, *Report on critical raw materials for the EU*, 2010.

9 J. Cui and L. Zhang, *J. Hazard. Mater.*, 2008, **158**, 228–56.

10 M. Karvelas, A. Katsoyiannis and C. Samara, *Chemosphere*, 2003, **53**, 1201–1210.

11 B. Bergbäck, K. Johansson and U. Mohlander, *Water, Air Soil Pollut. Focus*, **1**, 3–24.

12 R. Semiat, *Water Int.*, 2000, **25**, 54–65.

13 L. Henthorne, T. Pankratz and S. Murphy, in *Desalination: Sustainable solutions for a thirsty planet*, 2011, p. 6.

14 M. A. Darwish, F. M. Al Awadhi and M. Y. Abdul Raheem, *Desalin. Water Treat.*, 2010, **22**, 193–203.

15 A. H. Galama, in *Ion exchange membranes in seawater applications : processes and characteristics*, Wageningen University, Wageningen, 2015, p. 272.

16 A. Ophir and F. Lokiec, *Desalination*, 2005, **182**, 187–198.

17 M. Al-Sahali and H. Ettouney, *Desalination*, 2007, **214**, 227–240.

18 L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot and P. Moulin, *Water Res.*, 2009, **43**, 2317–48.

19 L. Malaeb and G. M. Ayoub, *Desalination*, 2011, **267**, 1–8.

20 C. Fritzmann, J. Löwenberg, T. Wintgens and T. Melin, *Desalination*, 2007, **216**, 1–76.

21 V. A. Shaposhnik and K. Kesore, *J. Memb. Sci.*, 1997, **136**, 35–39.

22 R. Audinos, *Chem. Eng. Technol.*, 1997, **20**, 247–258.

23 T. Xu and C. Huang, *AIChE J.*, 2008, **54**, 3147–3159.

24 H. Strathmann, *Ion-Exchange Membrane Separation Processes*, Elsevier B.V., Amsterdam, 9th edn., 2001.

25 A. H. Galama, J. W. Post, M. A. Cohen Stuart and P. M. Biesheuvel, *J. Memb. Sci.*, 2013, **442**, 131–139.

26 S.-Y. Kang, J.-U. Lee, S.-H. Moon and K.-W. Kim, *Chemosphere*, 2004, **56**, 141–7.

27 F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407–418.

28 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

29 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73–80.

30 K. . Marsh, J. . Boxall and R. Lichtenthaler, *Fluid Phase Equilib.*, 2004, **219**, 93–98.

31 D. M. Fox, W. H. Awad, J. W. Gilman, P. H. Maupin, H. C. De Long and P. C. Trulove, *Green Chem.*, 2003, **5**, 724–727.

32 B. Chan, N. Chang and M. Grimmett, *Aust. J. Chem.*, 1977, **30**, 2005–2013.

33 C. Maton, N. De Vos and C. V Stevens, *Chem. Soc. Rev.*, 2013, **42**, 5963–77.

34 J. L. Anderson and D. W. Armstrong, *Anal. Chem.*, 2003, **75**, 4851–4858.

35 D. Coleman and N. Gathergood, *Chem. Soc. Rev.*, 2010, **39**, 600–37.

36 T. P. T. Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–72.

37 M. Petkovic, J. L. Ferguson, H. Q. N. Gunaratne, R. Ferreira, M. C. Leitão, K. R. Seddon, L. P. N. Rebelo and C. S. Pereira, *Green Chem.*, 2010, **12**, 643.

38 M. D. Joshi and J. L. Anderson, *RSC Adv.*, 2012, **2**, 5470.

39 M. Althuluth, M. T. Mota-Martinez, A. Berrouk, M. C. Kroon and C. J. Peters, *J. Supercrit. Fluids*, 2014, **90**, 65–72.

40 G. E. Romanos, L. F. Zubeir, V. Likodimos, P. Falaras, M. C. Kroon, B. Iliev, G. Adamova and T. J. S. Schubert, *J. Phys. Chem. B*, 2013, **117**, 12234–51.

41 M. Abai, M. P. Atkins, A. Hassan, J. D. Holbrey, Y. Kuah, P. Nockemann, A. A. Oliferenko, N. V Plechkova, S. Rafeen, A. A. Rahman, R. Ramli, S. M. Shariff, K. R. Seddon, G. Srinivasan and Y. Zou, *Dalton Trans.*, 2015, **44**, 8617–24.

42 M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–9.

43 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.

44 P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978–20992.

45 T. Vander Hoogerstraete and K. Binnemans, *Green Chem.*, 2014, **16**, 1594–1606.

46 J. G. Huddleston and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.

47 H. Zhao, S. Xia and P. Ma, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1089–1096.

48 A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman and R. D. Rogers, *Sep. Sci. Technol.*, 2001, **36**, 785–804.

49 M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124–2125.

50 A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff and A. Wierzbicki, *Chem. Commun.*, 2001, 135–136.

51 D. S. Flett, *J. Organomet. Chem.*, 2005, **690**, 2426–2438.

52 M. . Jha, V. Kumar and R. . Singh, *Resour. Conserv. Recycl.*, 2001, **33**, 1–22.

53 L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water Res.*, 2011, **45**, 4601–4614.

54 J. F. Brennecke and E. J. Maginn, *AIChE J.*, 2001, **47**, 2384–2389.

55 S. Wellens, R. Goovaerts, C. Moeller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.

56 B. Weyershausen and K. Lehmann, *Green Chem.*, 2005, **7**, 15.

57 G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacha, T. Röder and H. Sixta, *Lenzinger Berichte*, 2005, **84**, 71–85.

58 H. Zhao, *Chem. Eng. Commun.*, 2006, **193**, 1660–1677.

59 D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 2150–2163.

60 D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 856–868.

61 J. R. Harjani, T. Friščić, L. R. MacGillivray and R. D. Singer, *Dalt. Trans.*, 2008, 4595.

62 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.

63 X. Sun, Y. Ji, F. Hu, B. He, J. Chen and D. Li, *Talanta*, 2010, **81**, 1877–83.

64 A. Rout and K. Binnemans, *Dalt. Trans.*, 2014, **43**, 1862–1872.

65 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Solvent Extr. ion Exch.*, 2011, **19**, 602–618.

66 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.

67 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.

68 J.-M. Lee, *Fluid Phase Equilib.*, 2012, **319**, 30–36.

69 M. Petkovic, K. R. Seddon, L. P. N. Rebelo and C. Silva Pereira, *Chem. Soc. Rev.*, 2011, **40**, 1383–403.

70 S.-K. Mikkola, A. Robciuc, J. Lokajová, A. J. Holding, M. Lämmerhofer, I. Kilpeläinen, J. M. Holopainen, A. W. T. King and S. K. Wiedmer, *Environ. Sci. Technol.*, 2015, **49**, 1870–1878.

71 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.

72 M. Regel-Rosocka and M. Wisniewski, *Hydrometallurgy*, 2011, **110**, 85–90.

73 M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young and M. P. Jensen, *Green Chem.*, 2003, **5**, 682.

74 V. A. Cocalia, J. D. Holbrey, K. E. Gutowski, N. J. Bridges and R. D. Roqers, *Tsinghua Sci. Technol.*, 2006, **11**, 188–193.

75 M. P. Jensen, J. Neuefeind, J. V Beitz, S. Skanthakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2003, **125**, 15466–73.

76 I. Billard, A. Ouadi and C. Gaillard, *Anal. Bioanal. Chem.*, 2011, **400**, 1555–1566.

77 M. Regel-rosocka and M. Wisniewski, *Appl. Ion. Liq. Sci. Technol.*, 2011, 375–398.

78 D. Kogelnig, A. Stojanovic, F. Jirsa, W. Körner, R. Krachler and B. K. Keppler, *Sep. Purif. Technol.*, 2010, **72**, 56–60.

79 M. Regel-Rosocka, *Sep. Purif. Technol.*, 2009, **66**, 19–24.

80 D. Zhang, W. Wang, Y. Deng, J. Zhang, H. Zhao and J. Chen, *Chem. Eng. J.*, 2012, **179**, 19–25.

81 X. Sun, Y. Ji, L. Zhang, J. Chen and D. Li, *J. Hazard. Mater.*, 2010, **182**, 447–52.

82 W. Wang, H. Yang, H. Cui, D. Zhang, Y. Liu and J. Chen, *Ind. Eng. Chem. Res.*, 2011, **50**, 7534–7541.

83 J. S. Preston, *Hydrometallurgy*, 1985, **14**, 171–188.

84 J. S. Preston, *Hydrometallurgy*, 1983, **11**, 105–124.

85 J. S. Preston and A. C. du Preez, *J. Chem. Technol. Biotechnol.*, 1994, **61**, 159–165.

86 F. Miller, *Talanta*, 1974, **21**, 685–703.

87 D. K. Singh, H. Singh and J. N. Mathur, *Hydrometallurgy*, 2006, **81**, 174–181.

88 C.-B. Xia, Y.-Z. Yang, X.-M. Xin and S.-X. Wang, *J. Radioanal. Nucl. Chem.*, 2008.

89 A. Cieszyńska, M. Regel-Rosocka and M. Wiśniewski, *Polish J. Chem. Technol.*, 2007, **9**, 99–101.

90 V. Gallardo, R. Navarro, I. Saucedo, M. Ávila and E. Guibal, *Sep. Sci. Technol.*, 2008, **43**, 2434–2459.

91 E. Guibal, K. C. Gavilan, P. Bunio, T. Vincent and A. Trochimczuk, *Sep. Sci. Technol.*, 2008, **43**, 2406–2433.

92 A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2010, **73**, 202–207.

93 F. G. Seeley and D. J. Crouse, *J. Chem. Eng. Data*, 1966, **11**, 424–429.

94 T. Sato and M. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 90–94.

95 T. Sato, M. Yamamoto and K. Sato, *Solvent Extr. Res. Dev. Japan*, 2005, **12**, 101–112.

96 T. Sato, M. Yamamoto and K. Adachi, *J. Min. Mater. Process. Inst. Japan*, 2005, **121**, 603–607.

97 K. Miyashita, E. Nara and T. Ota, *Biosci. Biotechnol. Biochem.*, 2014, **57**, 1638–1640.

98 R. A. Ferrari, V. da S. Oliveira and A. Scabio, *Sci. Agric.*, 2005, **62**, 291–295.

99 S. I. El Dessouky, Y. A. El-Nadi, I. M. Ahmed, E. A. Saad and J. A. Daoud, *Chem. Eng. Process. Process Intensif.*, 2008, **47**, 177–183.

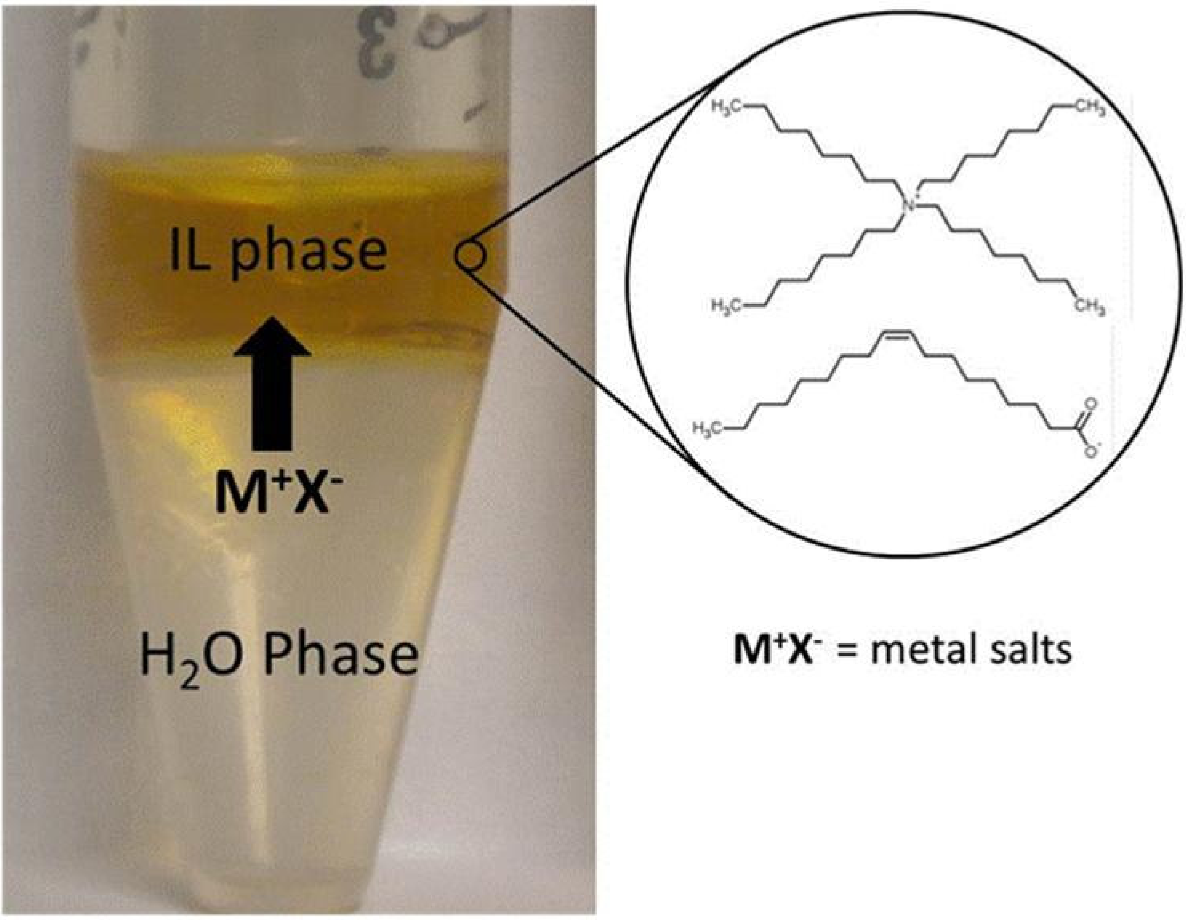
100 T. Fujii, F. Moynier, P. Telouk and M. Abe, *J. Phys. Chem. A*, 2010, **114**, 2543–52.

101 M. Regel, A. M. Sastre and J. Szymanowski, *Environ. Sci. Technol.*, 2001, **35**, 630–635.

102 M. Bartkowska, M. Regel-Rosocka and J. Szymanowski, *Chem. Technol.*, 2002, **36**, 217–224.

Chapter 2

Selecting a suitable ionic liquid



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2.1. Introduction

The chemical and mining industries have produced numerous aqueous streams polluted with valuable (heavy) metal salts.[1] As a result, groundwater is often polluted with these salts. Economically and technically, it is challenging to remove these impurities from the aqueous phase. Furthermore, also in industrial metal extraction process it is difficult to selectively separate the different metal salts.[2] Conventional methods to selectively recover and purify these metals use either volatile organic solvents, non-reusable absorbents, or harmful chemicals, such as sulfuric acid and cyanex, or a combination of these.[3,4,5]

Liquid-liquid extraction is one of the most important techniques for metal ion separation. As well as in the laboratory as on an industrial scale it offers several advantages over competing techniques.[2] Operation in a continuous mode, employment of relatively simple equipment and the employment of only small quantities of reagent are only some of these advantages. Biggest disadvantage of classical liquid-liquid extraction is the use of flammable, volatile or toxic water-immiscible organic solvents. One of the possibilities to improve the sustainability of this process is the use of ionic liquids (ILs) as water-immiscible extractants.[6,7]

ILs are defined as organic salts formed by the combination of bulky organic cations with a wide variety of anions that are liquid at room temperature.[8,9] Whereas classical solvents are made of neutral molecules, ILs are made of large ions, which are held together by electrostatic interactions. Because of these interactions, the properties of ILs are considerably different from those of molecular liquids. They have a wide liquid range, a negligible vapor pressure at room temperature, and a high chemical and electrochemical stability.[10]

Recently, the deployment of ILs as extracting agents for the recovery of valuable metals from waste water has become an interesting alternative for waste water plants.[11] This has been done in two different ways. The first option is based on using special extractants (e.g. crown ethers, cyanex) to extract the metals from the aqueous phase into the IL phase.[12,13,14,15] However, in these systems also ion exchange occurs: the uptake of the metal ion is accompanied by dissolution of the cation from the ionic liquid into the aqueous phase.[16] A preferred option is to use task-specific ionic liquids (TSILs) as extractants which are not prone to ion exchange.[17,18,19,20,21] These ILs have an ion that has a functionality that favours interaction with metal ions. In the literature, the focus on TSILs for metal extraction is prominent for ILs with carboxylic acid, phosphinic acid, thiourea, urea, thioether, and thiol functionalities in their ions.

In this work, TSILs with unsaturated fatty acids were for the first time synthesized and evaluated for their salt extraction capabilities. Metal extraction functionalities for these anions are their double bond(s) together with their carboxylic group. From earlier research it was already known that the unsaturated fatty acids allowed removal of heavy metals, ammonium, and rare earth metals in a wide range of concentrations.[22] On the other hand, unsaturated fatty acid soaps in combination with organic solvents and NaCl were also already used to extract europium (Eu^{3+}) via a microemulsion system.[23] Disadvantage was that both processes were based on cation exchange, in which sodium or calcium ions were replaced by other metal ions. This made chemical regeneration necessary and this was done by adding sulfuric acid to form a metal sulfate, followed by the addition of sodium/calcium hydroxide to form the fatty acid soap again. In these articles, it was mentioned that the carboxylic group[22,23] hydrophobisation effect[22] and microemulsion formation[23] have a large influence on the metal extraction using unsaturated fatty acids. On the other hand it is already shown that the π–electrons of the double bounds show good d-orbital metal interactions.[24] These interactions are even strengthened because, in addition to σ-bond interaction, there is also π-back donation.[24]

By working with fatty acid based TSIL we want to obtain full metal extraction so that the water phase is not polluted with (less harmful) ions and we want to avoid the use of chemical regeneration. The use of these anions, which are natural and biodegradable, for IL synthesis also brings us a step closer in making ILs more environmentally acceptable for industrial applications.[25] Highly hydrophobic cations, with very low water solubility, were chosen as counter ions to minimize ion exchange and to maximize metal extraction.

2.2. Experimental

Materials

The ILs used in this research were synthesized with reagents purchased from Sigma-Aldrich. Linoleic and oleic acid had a purity of ≥99%. Tetraoctylammonium chloride and methyltrioctylammonium chloride had a purity of 98% and 97%, respectively. Sodium hydroxide and ethanol (70%) were obtained from VWR-Prolabo®, and Toluene chromosolv® for HPLC (99%) was purchased from Sigma-Aldrich. MilliQ water (18.2MΩ.cm) used throughout the synthesis was obtained by a Millipore Milli-Q® biocel, which used a Q-grade® column. All chemicals were used as received, without any additional purification step. For composing the standard metal solutions, anhydrous LiCl(99%) was obtained from Sigma-

Aldrich. NaCl(>99.9%), KCl(>99.9%), $ZnCl_2$(98%), $FeCl_2.4H_2O$(≥99.0%), and $MnCl_2.2H_2O$(99%) were purchased from VWR-Prolabo®.

Synthesis

Four ILs, i.e. tetraoctylammonium linoleate ($[N_{8888}]$[linoleate]), methyltrioctylammonium oleate ($[N_{8881}]$[oleate]), methyltrioctylammonium linoleate ($[N_{8881}]$[linoleate]) and tetraoctylammonium oleate ($[N_{8888}]$[oleate]), were synthesized at the same experimental conditions by a two-step synthesis (Fig. 2.1.). First, sodium fatty acid was made by adding an equimolar amount of sodium hydroxide to the fatty acid dissolved in ethanol by stirring it overnight at room temperature. Afterwards, a metathesis reaction, for 3h at room temperature, was performed between the tetraalkylammonium chloride, dissolved in toluene and water, and the sodium fatty acid. A viscous liquid was obtained after purification of the organic phase. Detailed synthesis of the four ILs can be found in the supplementary information.

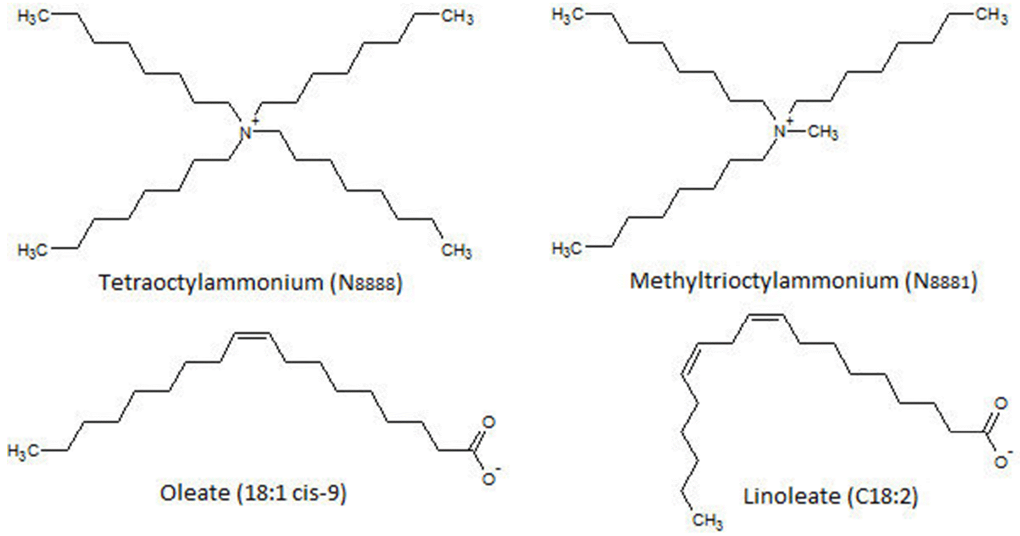


***Figure 2.1**. Ions that were used to synthesize the highly hydrophobic ionic liquids used in this article.*

Analysis

Analyses of our synthesized end products were performed on a 400 Brucker nuclear magnetic resonance (NMR) for ^1H NMR. Density and viscosity measurements were carried out on an Anton Paar SVM 3000/G2 type stabinger, with an uncertainty of +/- 0.0005 g/cm^3 for the density, +/- 0.005 mPa·s for the viscosity, and +/- 0.01 K for the temperature. Differential scanning calorimetry (DSC) Q 1000, and Perkin Elmer Pyris 1 were used to obtain the melting temperature with a scan rate of 10 °C min^{-1}. Decomposition temperatures were measured with a thermo-gravimetric analysis (TGA) Q 500 apparatus at a scan rate of 10 °C min^{-1} under a nitrogen flow. The spectra were analysed with TG instruments software. Determination of chloride impurities was done via ion chromatography (IC) as previously described,[26] but problems occurred during this technique. The described procedure to prepare the IC sample by dissolving 1.1 g of IL in 2 mL acetonitrile before being diluted to 10 mL with water resulted in a phase separation. IC samples with less IL resulted in malfunction of the IC. Finally, the chloride content was determined to be negligibly low by washing with water and checking that no AgCl precipitate was formed after $AgNO_3$ addition. The water content of the ILs were determined by a coulometric Karl Fischer titrator (Mettler Toledo, model DL39).

Experimental salt extraction procedure

First, two aqueous metal solutions were prepared. The group I (alkali) metal solution consists of LiCl, NaCl, and KCl. Of each of these salts, 1 gram was dissolved in 100mL demineralised water. For the aqueous solutions containing period IV metals, we dissolved 0.5 gram of $MnCl_2 \cdot 2H_2O$ together with 0.5 gram of $FeCl_2 \cdot 4H_2O$ and 0.5 gram of $ZnCl_2$ in 100mL demineralised water. The four ILs synthesized were tested for both alkali metal extraction and period IV metal salt extraction. One gram of the selected IL was divided equally over two centrifuge tubes. 0.5 mL of metal solution was added to one tube and to the other 0.5 mL demineralised water was added as a reference (blank). Both samples were stirred for 2h on a vortex mixer Heidolph multireax and afterwards placed in an Allegra TM X-12R centrifuge from Beckman coulter for 10 min at 3750 rpm. Afterwards, aqueous phases were analysed on IC and inductively coupled plasma (ICP) to detect if metal extraction was occurring. A Metrohom 761 Compact IC and 762 IC interface was used to analyse the anion concentration with a detection limit of 0.1 mg·L^{-1}. Cations were measured with a Perkin Elmer, precisely ICP, which used an optical emission spectrometer 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%.

Extraction efficiencies (E) were calculated by

$$E(\%) = \left(\frac{(c_{0aq} - c_{1aq})}{c_{0aq}}\right) \text{x } 100 \qquad (1)$$

where $c_0$aq and c_{1aq} are the total metal concentrations in the aqueous phase before and after the experiment, respectively.

Subsequently, electronspray-ionisation combined with mass spectrometry (ESI-MS) was used to detect whether ion exchange took place as well. In that case, part of our IL would dissolve in water after metal extraction. An Agilent Technologies 1200 series ESI-MS was used with acetonitrile:water 90:10 v/v as eluens working with an Agilent masshunter workstation data acquisition.

2.3. Results and Discussion

For this research, we first synthesized the ILs with fatty acid anions. To do this, tetraalkylammonium halide ILs were used in a metathesis reaction with the sodium salt of the fatty acids. The synthesis of these ILs was very simple and they were obtained in high (between 72 and 99%) yields. The physical properties of the synthesized ILs are outlined in Table 2.1. In the literature, it is mentioned that the density of ILs depends mostly on the molecular shape of the anion.[27] Fatty acids, which have already a low density, were used as anions. We assume that this is the reason why these ILs have, in contrast to common ILs, a density lower than water. Viscosities were found to be more dependent on the cationic structure.[28] Water and chloride are present in the synthetic route of these ILs and they can alter all the physical properties considerably.[29] Water is present, but chloride was not found to be a large impurity.

Table 2.1. *Density (ρ), dynamic viscosity (η) and kinematic viscosity (v) at 20 °C, melting temperature (T_m), decomposition temperature (T_d) and water content (w_{H2O}) of the applied ILs.*

ILs	Density[a] (ρ; g/cm^3)	dynamic viscosity[a] (η; mPa·s)	kinematic viscosity[a] (v; mm^2/s)	T_m (°C)	T_d (°C)	w_{H2O} (ppm)
[N_{8888}][linoleate]	0,883	1280	1450	<-60	170	6900
[N_{8881}][linoleate]	0,889	1047	1178	-37	150	9800
[N_{8888}][oleate]	0,875	1234	1410	<-60	175	7200
[N_{8881}][oleate]	0,884	1321	1494	-25	169	10880

The synthesized ILs were evaluated for their metal extraction performance. As a result of the extraction experiment, a promising colour change was noticed for the ILs after they were mixed with the period IV metal solution (Fig. 2.2). No colour change was noticed for the

ILs when they were mixed with the aqueous group I metal solution. A comparison of the aqueous metal concentrations was done for all four ILs after each extraction experiment. The extraction efficiencies of the ILs for the specific metals can be found in Table 2.2 for the alkali metal salts and in Table 2.3 for the period IV metal salts.

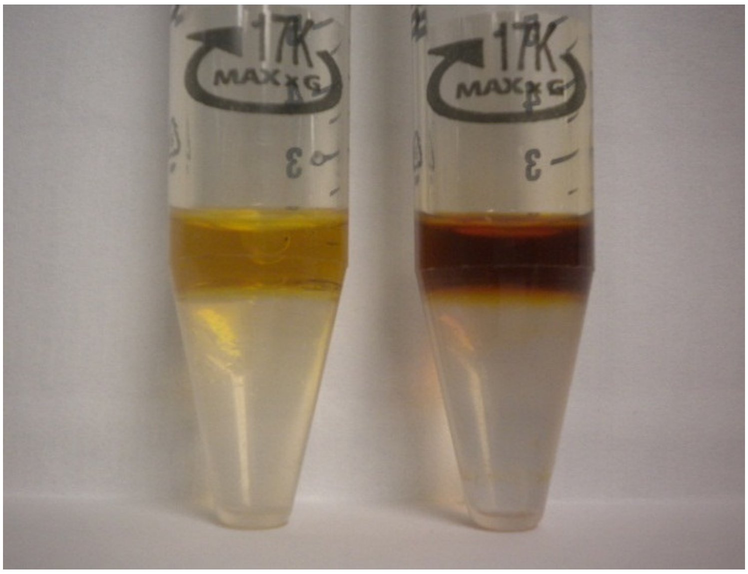


Figure 2.2. *Colour change observed during period IV metal extraction. The first tube shows us the IL tetraoctylammonium linoleate before metal extraction is shown (left). In the second tube we observe the same IL after metal extraction (right).*

No significant reductions in ion concentrations were observed when the ILs were mixed with the group I metal solution (Table 2.2). Only the oleate based ILs showed a minor reduction of lithium as well as a reduction of the chloride concentration. The reason why the reduction in total chloride concentration is smaller, is because the amount of total chloride is higher (the solution also contains NaCl and KCl). The extraction efficiency of sodium and potassium is 0%. However, in some experiments the concentration of sodium and potassium slightly increased (leading to negative extraction efficiencies up to -3%), which could be explained by the sodium hydroxide used during synthesis of the ILs, and potassium is a major impurity in sodium hydroxide.

Table 2.2. *Extraction efficiencies for all four ILs with the group I metal solution (phase ratio 1:1; 20 °C). [N_{8888}][linoleate] (E_1), [N_{8881}][oleate] (E_2), [N_{8881}][linoleate] (E_3), [N_{8888}][oleate] (E_4).*

	E_1 (%)	E_2 (%)	E_3 (%)	E_4 (%)
Chloride	0	11.7	0	2
Potassium	0	0	0	0
Sodium	0	0	0	0
Lithium	0	22.4	0	4

Table 2.3. *Extraction efficiencies for all four ILs with the period IV metal solution (phase ratio 1:1; 20 °C). [N_{8888}][linoleate] (E_1), [N_{8881}][oleate] (E_2), [N_{8881}][linoleate] (E_3), [N_{8888}][oleate] (E_4).*

	E_1 (%)	E_2 (%)	E_3 (%)	E_4 (%)
Chloride	89.5	84.1	73.1	90.8
Iron	88.8	96.5	71	98.4
Manganese	58.6	69.4	37.3	70.7
Zinc	99.8	94.9	99.6	99.8

Table 2.3. shows an enormous extraction efficiency (up to >99%) for iron and zinc using all four ILs. In addition, the concentration of manganese was significantly reduced (up to 71%). Comparison with extraction efficiencies with pure unsaturated fatty acids shows that the newly synthesized ILs perform equally well.[22] The influence of the anion in our ILs on the extraction efficiency was dominant. It was found that the linoleate based ILs show better extraction of zinc but, less extraction of iron and manganese compared to the oleate based ILs. The cation has a smaller influence on the extraction efficiency. The extraction efficiencies of methyltrioctylammonium based ILs are slightly lower than the ones of tetraoctylammonium based ILs. The high extraction of period IV transition metals is the reason for the colour change that was observed for all ILs. Together with the reduction of these metals, a reduction in chloride concentration was observed, which points out that for these systems ion extraction occurs instead of ion exchange.

A calculation was done to determine the ratio of extraction/ion-exchange. Therefore, we divided the theoretical concentration of chloride from the removed metal concentration (based on the observed cation extraction) by the observed removed concentration of chloride. These values ranged from 0.88 to 0.93. This means that ion-pair extraction is the dominant mechanism. There are 2 possible reasons why this value is slightly lower than 1 (indicating that more chloride than cations are extracted: (i) some ion exchange occurs, and (ii) oxidation of Fe(II) to Fe(III), followed by metal fatty acid complex formation. Oxidation of Fe(II) seems to be the most likely explanation, because over time a precipitate is formed indicating the occurrence of a chemical reaction. Moreover, ESI-MS results show that the concentration of the organic ions in the water phase is similarly low for the aqueous period IV metal ion solution compared to milliQ (blank) experiment after mixing with the ILs, indicating that no ion exchange occurs. Therefore, this process is a green alternative for metal extraction from aqueous phases.

It should be mentioned that after the extraction experiment we always detect some low organic ion concentrations in the water phase. Methyltrioctyl ammonium based ILs were even able to form an emulsion with distilled water (blank) under vigorous shaking, while the tetraoctylammonium based ILs fortunately did not form an emulsion with the blank as well as with the metal solutions. Probably the asymmetry of the cation favours emulsion formation. ESI-MS results confirmed an increase of the cation methyltrioctylammonium in the water phase after emulsion formation by vigorous shaking. For this reason, it is obvious that the ions for the used ILs have to be biocompatible, non-toxic, and highly hydrophobic.

The challenge now is to sustainably regenerate the ILs. With sustainable we mean that the regeneration should be less electric energy consuming then current metal extraction processes and are performed without the use of toxic chemicals. Electrodeposition and cementation look very promising for this task. Especially, if one could remove the different metals separately out of the ILs.

2.4. Conclusions

Ionic liquids with unsaturated fatty acids as anions were easily synthesized via a metathesis reaction. The advantages of these ILs are their simple synthesis, their sustainability (fatty acids anions are renewable), their biocompatibility and their non-toxicity. This makes these ILs “simpler and greener” compared to other TSILs used for metal extraction. While they showed no or negligible extraction efficiencies for alkali metal salts, very good extraction efficiencies (>99%) were observed for the period IV transition metal salts. The extraction process was based on ion extraction instead of ion exchange, which minimized IL leakages into the water phase.

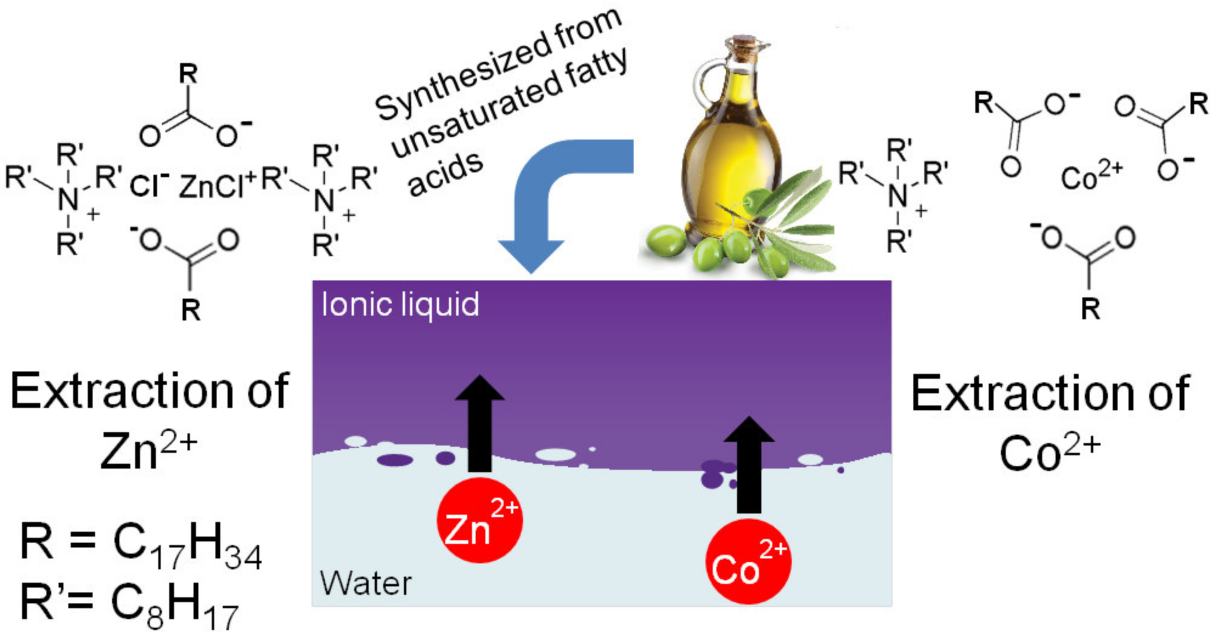
Further research is necessary to regenerate these ILs with electrodeposition or cementation. This would result in a very sustainable process to remove heavy metal salts form aqueous water solutions.

2.5. References

1. J.F. Blais, Z. Djedidi, R. Ben Cheikh, R.D. Tyagi, G. Mercier, *J. Hazard., Toxic, Radioact. Waste* **2008,** *12* (3), 135-149.
2. S. Wellens, B. Thijs, K. Binnemans, *Green Chemistry* **2012,** ***14***, 1657-1665.
3. N.B. Devi, K. C. Nathsarma, V. Chakravortty, *Hydrometallurgy* **1998,** *49* (1-2), 47-61.
4. J. G. Dean, F.L. Bosqui, K.H. Lanouette, *Environ. Sci. Technol.* **1972,** *6* (6), 518-522.
5. A.G. Chmielewski, T.S. Urbanski, W. Migdal, *Hydrometallurgy* **1997,** *45* (3), 333-344.
6. M.L. Dietz, *Separ. Sci. Technol.* **2006,** *41* (10), 2047-2063.
7. G. Huddleston, D. Rogers, *Chem. Commun.* **1998,** (16), 1765-1766.
8. J.P. Hallett, T. Welton, *Chem. Rev.* **2011,** *111* (5), 3508-3576.
9. U. Domańska, R. Bogel-lukasik, *J. Phys. Chem. B* **2005,** *109* (24), 12124-12132.
10. J. S. Wilkes, *Green Chem.* **2002,** *4* (2), 73-80.
11. A. P. Abbott, G. Frisch, J. Hartley, K. S. Ryder, *Green Chem.* **2011,** *13* (3), 471-481.
12. V. A. Cocalia, J. D. Holbrey, K. E. Gutowski, N. J. Bridges, R. D. Rogers, *Tsinghua Sci. Technol.* **2006,** *11* (2), 188-193.
13. X. Sun, Y. Ji, L. Guo, J. Chen, D. Li, *Sep.. Purif. Technol.* **2011,** *81* (1), 25-30.
14. A. E. Visser, R. D. Rogers, *J. Solid State Chem. 171* (1-2), 109-113.
15. A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman, R. D. Rogers, *Separ. Sci. Technol.* **2001,** *36* (5-6), 785-804.
16. M. L. Dietz, D. C. Stepinski, *Green Chem.* **2005,** *7* (10), 747-750.
17. Z. Li, Q. Wei, R. Yuan, X. Zhou, H. Liu, H. Shan, Q. Song, *Talanta* **2007,** *71* (1), 68-72.
18. J. R. Harjani, T. Friscic, L. R. MacGillivray, R. D. Singer, *Dalton Trans.* **2008,** (34), 4595-4601.
19. P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner, K. Binnemans, *J. Phys. Chem. B* **2006,** *110* (42), 20978-20992.
20. X. Sun, Y. Ji, F. Hu, B. He, J. Chen, D. Li, *Talanta* **2010,** *81* (4-5), 1877-1883.
21. L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler, S. Hann, *Water Research* **2011,** *45* (15), 4601-4614.
22. J. Šiška, *Hydrometallurgy* **2005,** *76* (3-4), 155-172.
23. W. Wang, Y. Yang, H. Zhao, Q. Guo, W. Lu, Y. Lu, *J. Radioanal. Nucl. Chem.* **2012**, 292, 1093-1098
24. H. Zhao, A. Ariafard, Z. Lin, *Inorg. Chim. Acta.* **2006,** *359* (11), 3527-3534.
25. M. Petkovic, K. R. Seddon, L. P. Rebelo, C. S. Pereira, *Chem. Soc. Rev.* **2011,** *40* (3), 1383-1403.
26. C. Villagrán, M. Deetlefs, W. R.Pitner, C. Hardacre, *Anal. Chem.* **2004,** *76* (7), 2118-2123.
27. S. Seki, T. Kobayashi, Y. Kobayashi, K. Takei, H. Miyashiro, K. Hayamizu, S. Tsuzuki, T. Mitsugi, Y. Umebayashi, *J. Mol. Liq.* **2010,** *152* (1-3), 9-13.
28. P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA: 2007; p i-xxv.
29. K. R. Seddon, A. Stark, M. J. Torres, *Pure Appl. Chem.* **2000,** *72* (12), 2275-2287.

Chapter 3

Mechanism of metal extraction



3.1. Introduction

The chemical, metallurgical and mining industries produce large volumes of aqueous streams contaminated by valuable (heavy and light) metal salts. The existing conventional methods to selectively recover these metal salts use volatile organic solvents and harmful chemicals, such as aliphatic hydrocarbons, sulphuric acid and organophosphorus extractants.[5152] Therefore, it is necessary to develop new methods that selectively extract metal salts and purify water in a more economically and environmentally friendly way. Research pointed out that ionic liquids (ILs) are interesting alternative solvents to overcome above mentioned problems.[48,53]

ILs have a large potential for a wide variety of applications in the chemical industry due to their interesting properties.[28,54–60] 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 temperature range. Moreover, ILs can be specifically designed for metal extraction by choosing a suitable cation and anion.[61–68] Two main disadvantages of using ILs are their toxicity in direct contact of eyes, skin, and the respiratory system and their poor biodegradability.[35,69,70] 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. Recently, progress was made by developing natural fatty acid based ILs (tetraalkylammonium oleate and tetraalkylammonium linoleate).[71]

Previously, several studies investigated the metal extraction mechanism of ILs in combination with an extractant.[72–75] The extraction of metals in these IL can proceed in three different ways (1) ion-pair extraction; which is the extraction of the metal cations with the corresponding anions from the water phase towards the IL phase; (2) ion exchange; in which anions or cations from the IL or the extractant 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.[76]

Metal salt extraction with extractants dissolved in ILs is sometimes accompanied by an increasing dissolution of the IL into the aqueous phase (mechanism 2), which cannot be regarded as environmentally friendly.[49] In this research, ion exchange during metal extraction was avoided by selecting a large hydrophobic symmetrical cation, tetraoctylammonium, in combination with a hydrophobic fatty acid anion.

The mechanism of salt extraction in case of undiluted non-fluorinated hydrophobic ILs has already been reported.[77] For example, hydrophobic tetraalkylammonium or tetraalkylphosphonium based chloride ILs are able to extract 3d transition metal ions as tetrachloro complexes.[78,79] The mechanism for the extraction of metals using undiluted bifunctional ILs, i.e. ILs which are combinations of organic acids and organic bases that both have the ability to extract metals towards the IL phase, has been reported. This extraction mechanism is based on the coordination of one or more IL molecules towards the metal cation from which then together with the anion of the metal salt a charge neutral IL metal complex is formed.[63,80–82] For example, the extraction mechanism of cobalt sulphate by [tricaprylmethylammonium][sec-octylphenoxy acetate] ([A336][CA-12]) is by slope analysis defined as the interaction of 1 Co^{2+} ion with 1 IL molecule. In this mechanism one adds also the extraction of sulphate to keep the complex charge neutral. The extraction mechanism is based on ion-pair extraction.[81]

$$Co_{aq}^{2+} + SO_4^{2-} + [A336][CA{:}12]_{org} \rightleftharpoons [Co^{2+}][SO_4^{2+}][A336][CA{:}12]_{org} \tag{1}$$

Tetraalkylammonium oleate belongs to this group of ILs and in the present work, the metal extraction process for the first row (3d) transition metals Zn(II), Co(II) and Ni(II) from their respective chloride salts has been investigated. This allows a better understanding of the metal ion removal from the aqueous phase with this type of ILs. Insight into the mechanism is useful for further development of more environmentally friendly ILs, used for selective salt extraction, salt recovery and solvent reusability.

3.2. Experimental

Materials

Tetraoctylammonium oleate ($[N_{8888}]$[oleate]), see Figure 3.1, was synthesized as described in detail elsewhere.[71] Boom B.V. (Meppel, The Netherlands) supplied manganese(II) chloride dehydrate (99%), nickel(II) chloride hexahydrate (99%) and perchloric acid (70%). Zinc(II) chloride (99,99%) 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). MilliQ water (≥18 MΩ·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.

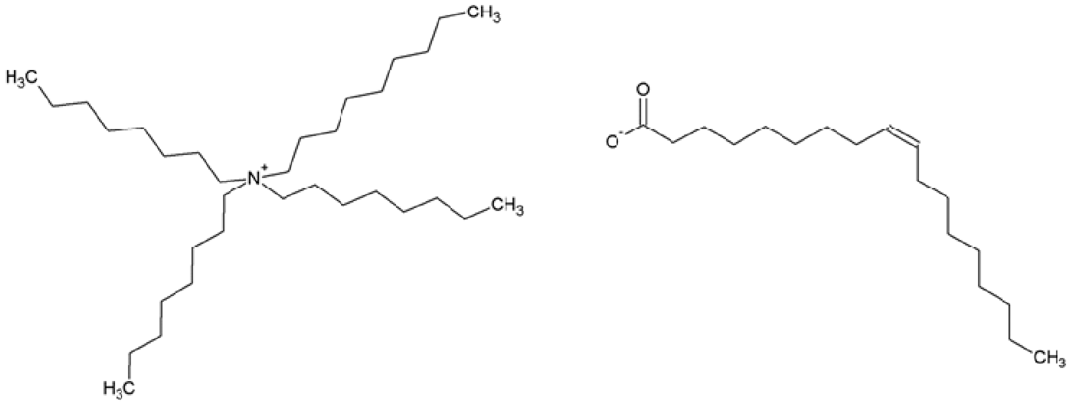


Figure 3.1. *Structure of [N_{8888}][oleate].*

Experimental salt extraction procedure

A standard salt solution was prepared by dissolving 0.5 g of each salt ($ZnCl_2$, $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$) in 100 mL of Milli-Q water (pH = 6.33). Then, 1 mL of the 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 room temperature (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. To investigate the metal extraction potential of the IL compared to the precursors, the extraction was performed (1) with 1 g of tetraoctylammonium oleate, (2) with 1 g of oleic acid, (3) with 1 g of tetraoctylammonium chloride and (4) with 0.4 g of sodium oleate dissolved in 0.6 g of oleic acid.

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

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

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

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 atomic emission spectroscopy (ICP-

AES). A Metrohm 761 Compact IC and 762 IC interface 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 $NaHCO_3$ aqueous solution + 1% acetone + 5 μM KIO_3) and regenerated with suppressor liquids (100 mM sulphuric acid + 1% acetone in Milli-Q water). Cations were measured with a Perkin Elmer ICP, which used an optical emission spectrometer Optima 5300 DV. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-AES has a detection limit of 50 μg·L^{-1}, with an uncertainty of 2%. The pH of the water phase was measured after the metal extraction experiment with a Metrohm 827pH lab.

Slope analysis

Slope analysis experiments with a changing IL concentration were performed with single element solutions of $CoCl_2$, $NiCl_2$ and $ZnCl_2$. Diluted solutions of the different metal chloride salts (500 ppm) were selected in order to maintain the pH in the same range. For this experiment, 3.5 g of IL was dissolved in 100 mL of toluene. Then, 1 mL of the aqueous metal solutions was mixed with different volumes 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 constant IL concentration 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 $CoCl_2$ solution or $NiCl_2$ solution. Then, different volumes of a 37 wt% HCl solution were added to the mixtures. These solutions were then 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.

3.3. Results and discussion

Metal chloride extraction: the IL in comparison with its precursors

First, the extraction performance for 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) were compared with the extraction when using the pure IL

(Table 3.1). From Table 3.1, 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 as expected, because commercially used carboxylic acids (e.g. Versatic Acid) have similar extraction properties as the oleate anion.[83–87] Literature indicated that metal extraction with Versatic Acid 10 and oleic acid occurs via the formation of a metal carboxylate (1:2) complex and that the extraction is highly pH dependent.[88]

Zn(II) is extracted with sodium oleate, tetraoctylammonium chloride and the IL (Table 3.1). 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 than the one used in this work, is a popular extraction agent for transition metals.[72,78,89–92] The extraction of these metals by this agent occurs always in the form of metal chloro complexes and therefore, the extraction efficiency depends on the stability of the chloro complexes. For most of the metals, high chloride concentrations (e.g. 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 low chloride concentrations.[63,93]

Table 3.1. *Distribution ratios of $CoCl_2$, $NiCl_2$ and $ZnCl_2$ with $[N_{8888}]$[oleate], oleic acid, tetraoctylammonium chloride ($[N_{8888}]$[Cl]) and sodium oleate ([Na][oleate]).*

	$[N_{8888}]$[oleate]	*oleic acid*	*$[N_{8888}]$[Cl]*	*[Na][oleate]*
Chloride	4750	0.00	1850	0.00
Cobalt	20.4	0.05	0.06	210
Nickel	13.5	0.05	0.03	211
Zinc	183	0.15	22.8	219

Finally, from Table 3.1, it can be observed that chloride extraction does not take place using sodium oleate as extractant, because the extraction mechanism here is fully based on the ion exchange of sodium for multivalent metal ions. This is different from the extraction with the IL where there is, next to the extraction of the metal cation, also chloride extraction, indicating that a different mechanism takes place (no ion exchange, but 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 extraction mechanism via slope analysis

Sato et al. described the extraction mechanism for divalent transition metals by long-chain alkyl quaternary ammonium carboxylates as (Equation 3):[94–96]

$$M^{2+}_{aq} + 2Cl^{-}_{aq} + 3\overline{[N^{+}_{xywz}][R'COO^{-}]} \rightleftharpoons \overline{[N^{+}_{xywz}][M(R'COO)^{-}_{3}]} + 2\overline{[N^{+}_{xywz}][Cl^{-}]} \qquad (3)$$

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

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

$$M^{2+}_{aq} + 2Cl^{-}_{aq} + 3\overline{[N^{+}_{8888}][oleate^{-}]} \rightleftharpoons \overline{[N^{+}_{8888}][M(oleate)^{-}_{3}]} + 2\overline{[N^{+}_{8888}][Cl^{-}]} \qquad (4)$$

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

$$K_{ext} = \frac{\overline{[N^{+}_{8888}][M(oleate)^{-}_{3}]}\left(\overline{[N^{+}_{8888}][Cl^{-}]}\right)^{2}}{\left(\overline{[N^{+}_{8888}][oleate^{-}]}\right)^{3}[Cl^{-}]^{2}[M^{2+}]} \qquad (5)$$

This equation can be further simplified because of the expected ion-pair extraction mechanism.[71] Therefore, the remaining chloride concentration $[Cl^{-}]_{aq}$ in the aqueous phase equals two times the $[M^{2+}]_{aq}$ concentration in the aqueous phase ($2[M^{2+}]_{aq} = [Cl^{-}]_{aq}$) and the concentration of chloride extracted as $[N^{+}_{8888}][Cl^{-}]$ equals two times the concentration of $[N^{+}_{8888}][M(oleate)^{-}_{3}]$ ($[N^{+}_{8888}][Cl^{-}] = 2\,[N^{+}_{8888}][M(oleate)^{-}_{3}]$). Equation (5) then becomes:

$$K_{ext} = \frac{\left(\overline{[N^{+}_{8888}][M(oleate)^{-}_{3}]}\right)^{3}}{\left(\overline{[N^{+}_{8888}][oleate^{-}]}\right)^{3}(M^{2+})^{3}} \qquad (6)$$

Insertion of *D,* defined in Equation (2), into Equation (6) and rewriting gives

$$\log D = \frac{n}{3}\log K + n\log\overline{[N^{+}_{8888}][oleate^{-}]} \qquad (7)$$

in which n equals the number of IL molecules involved in the extraction of one metal salt (MCl_2).

If three IL molecules are involved in the extraction, proposed by Equation (4), than one should obtain a slope of 1 if log *D* is plotted as a function of the IL concentration at constant pH value. Nickel(II) chloride ($NiCl_2$) was the first metal tested, because this metal is not forming very stable metal chloro complexes in the IL phase and can therefore only be extracted via the oleate anion of the IL (Figure 3.2).[80] Afterwards, a slope analysis was performed for $CoCl_2$, which is also extracted via the oleate anion, because extraction via the cation is only possible at high chloride concentrations (Figure 3.3). For these experiments, no acid or base was added to the aqueous phase. The experiments were performed by dissolving the IL in toluene in order to avoid volume changes and 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. Figure 3.2 and 3.3 show a linear relation between Log *D* and Log [IL]. The slope for $NiCl_2$ equals $y = 0.84x + 3.23$, with a 0.99 R^2-value of the fit and the slope for $CoCl_2$ is $y = 0.93x + 3.70$ with an R^2-value for the fit of 0.99. Both slope are close to 1 which is in agreement with Equation (4).

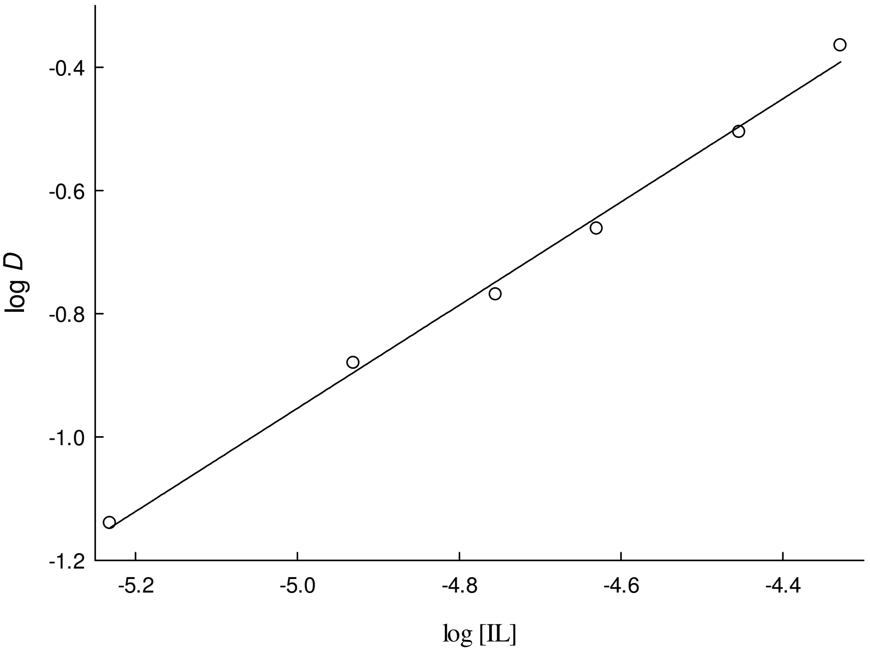


Figure 3.2. *Slope analysis for the extraction of $NiCl_2$ with $[N_{8888}]$[oleate] in toluene.*

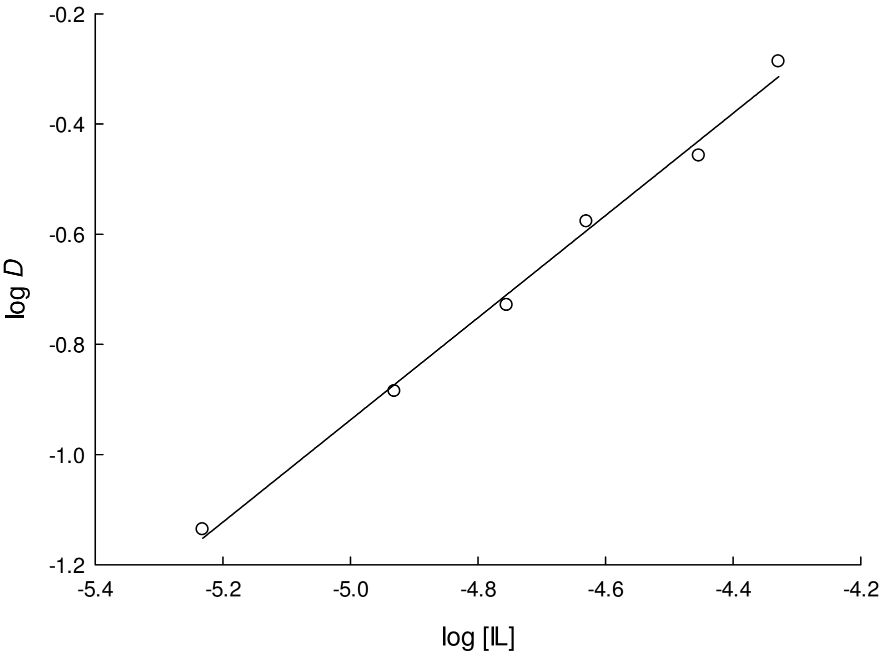


Figure 3.3. *Slope analysis for the extraction of CoCl$_2$ with [N$_{8888}$][oleate] in toluene.*

Adding acid to the IL leads to protonation of the anion. (Equation (9) in the case of hydrochloric acid) The results in Table 3.1 demonstrate that the protonated anion, oleic acid, does not extract metals. Therefore, it is expected that adding acid results in a decreased metal extraction.

$$H^+_{aq} + Cl^-_{aq} + \overline{[N^+_{8888}][oleate^-]} \rightleftharpoons \overline{[N^+_{8888}][Cl^-]} + \overline{oleic\ acid} \tag{9}$$

The lower the pH, the more IL anion gets protonated and the less metal that gets extracted. From a pH ≤ 7 no Co(II) and Ni(II) extraction is observed. Plotting log D as a function of the pH (Figure 3.4) show straight lines with a linear fit through the experimental data points for Co corresponding to $y = 2.81x - 20.42$, the R^2-value of the fit is 0.99 and for Ni the linear fit through the data equals $y = 3.11x - 28.89$, the R^2-value of the fit is 0.99. Both slopes are close to 3 and again suggest, as indicated in Equation (4), that 3 IL molecules are responsible for the metal extraction of Co(II) and Ni(II) when using the pure IL [N$_{8888}$][oleate].

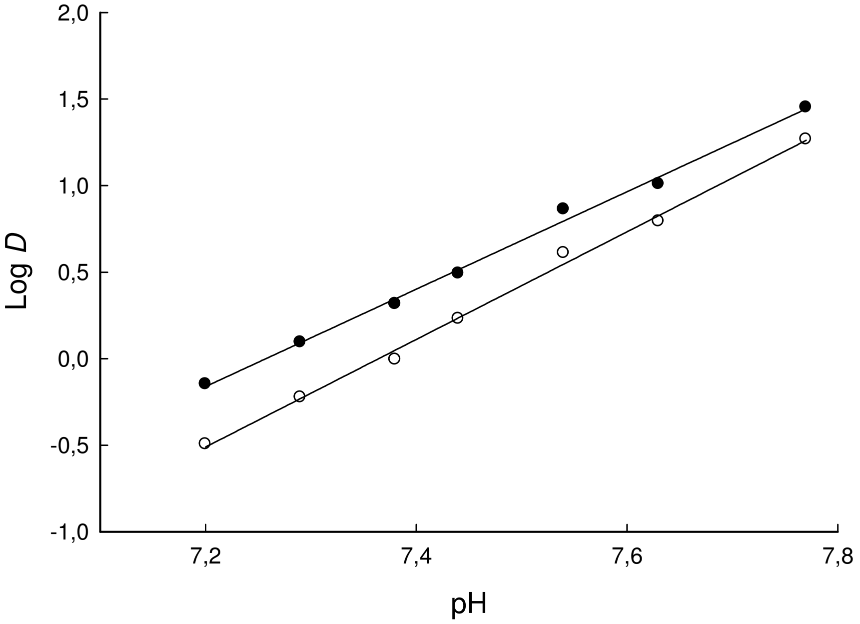


Figure 3.4. *Slope analysis for the extraction of $CoCl_2$ (●) and $NiCl_2$ (○) with [N_{8888}][oleate] as a function of the pH.*

It has to be reported that it was important to measure the pH of the slope analysis experiments always directly after the measurement. Small fluctuations of the pH were observed over time. A possible explanation for this observation is degradation of the anion of the IL, because it is known that unsaturated carboxylic acids can undergo catalyzed degradation at higher temperatures.[97,98] However no changes in the NMR spectra of the IL after extraction were observed after one month of storage, because it is assumed that the decomposition occurs in the concentration range of 10^{-6} to 10^{-7} M.

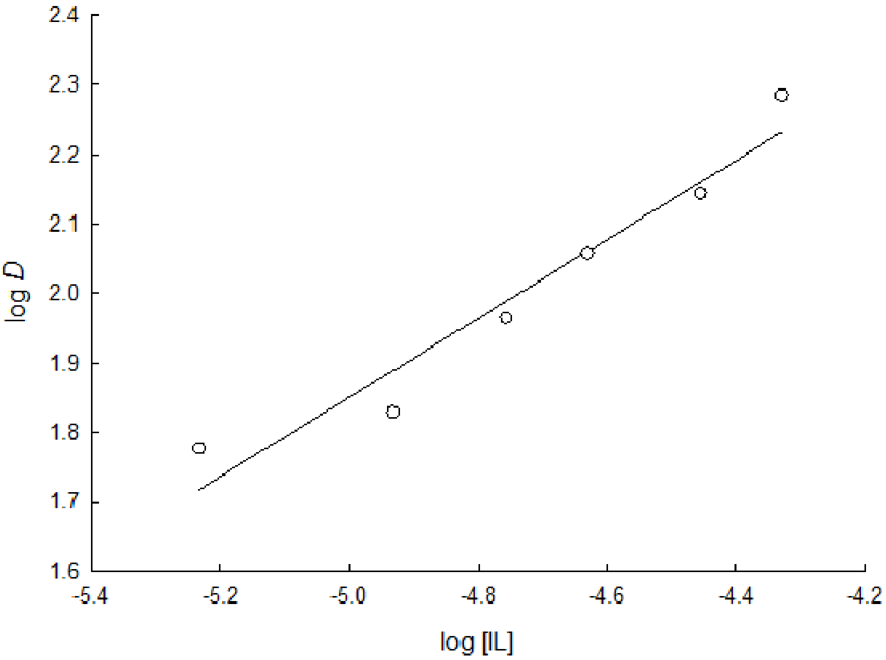


Figure 3.5. *Slope analysis for the extraction of* $ZnCl_2$ *with* $[N_{8888}]$*[oleate] in toluene.*

According to Sato *et al.,* Zn(II) has a similar extraction mechanism compared to the metals Ni(II) and Co(II).[94] Yet, from Table 3.1, 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 $y = 0.50x + 4.47$, with an R^2-value for the fit of 0.97 was obtained (Figure 3.5). It is known that Zn(II) can form different species in the aqueous phase in the presence of chloride ligands (Zn^{2+}, $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$ and $ZnCl_4^{2-}$) depending on the pH and chloride concentration.[99–102] 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.[96] In this specific case, the extraction of Cd(II) was found to occur via a $CdCl^+$ complex in combination with 2 IL molecules, see Equation 10.

$$MCl_{aq}^{+} + Cl_{aq}^{-} + 2\overline{[N_{xywz}^{+}][R'COO^{-}]} \rightleftharpoons \overline{[N_{xywz}^{+}]_2[MCl_2(R'COO)_2{}^{2-}]} \qquad (10)$$

The extraction constant (K_{ext}) defined for Equation 10 is:

$$K_{ext} = \frac{\overline{[N^+_{xywz}]_2\left[MCl_2(R'COO)_2{}^{2-}\right]}}{\left(\overline{[N^+_{xywz}][R'COO^-]}\right)^2[Cl^-][MCl^+]} \tag{11}$$

Substituting *D* defined in Equation (2) into Equation (11) and rewriting gives

$$\log D = \ n\log\mathrm{K}\ + 2n\log\overline{\left[N^+_{xywz}\right][R'COO^-]} + \ n\log[Cl^-] \tag{12}$$

As proposed by Equation (12), if two IL molecules are involved in the extraction than one should obtain a slope of 0.5 if log *D* is plotted as a function of the IL concentration at constant pH value. From Figure 3.5, it is assumed that, the following extraction mechanism is occurring for zinc:

$$ZnCl^+_{aq} + Cl^-_{aq} + 2\overline{[N^+_{8888}][oleate^-]} \rightleftharpoons \ \overline{[N^+_{8888}]_2\left[ZnCl_2(oleate)_2{}^{2-}\right]} \tag{13}$$

It was already observed from Table 3.1 that Zn has a much higher distribution ratio compared to Ni and Co. Chloride as ligand forms more stable complexes with metals compared to oleate. Therefore, it is assumed that the presence of the ZnCl complex in the IL metal complex makes that this complex has a higher stability compared to the Ni and Co IL complex. Resulting in the higher distribution ratio for Zn.

3.4. Conclusions

The extraction mechanism of the transition metal ions Co(II), Ni(II) and Zn(II) with the IL [N_{8888}][oleate] was investigated. For the metals Ni(II) and Co(II), it was observed that the metal extraction mechanism was based on a IL metal complex, in which both the anion as the cation stabilize the metal ion, i.e. $[N^+_{8888}][M(oleate)^-_3]$. This extraction mechanism is valid for Co(II) and Ni(II) chloride metals. Zn(II) was extracted via a different extraction mechanism, in which the Zn(II) ion is stabilized as a $ZnCl^+$ ion in an IL metal complex at the conditions that were applied, i.e. $[N^+_{8888}]_2\left[MCl_2(oleate)_2{}^{2-}\right]$ at pH 6.7 and without the addition of additional chloride sources. The presence of a very stable chloride ligand in the case of Zn compared to the oleate ligand results in the higher distribution ratio for Zn compared to Ni and Co.

3.5. References

1 J. P. Grotzinger, J. Crisp, A. R. Vasavada, R. C. Anderson, C. J. Baker, R. Barry, D. F. Blake, P. Conrad, K. S. Edgett, B. Ferdowski, R. Gellert, J. B. Gilbert, M. Golombek, J. Gómez-Elvira, D. M. Hassler, L. Jandura, M. Litvak, P. Mahaffy, J. Maki, M. Meyer, M. C. Malin, I. Mitrofanov, J. J. Simmonds, D. Vaniman, R. V. Welch and R. C. Wiens, *Space Sci. Rev.*, 2012, **170**, 5–56.

2 D. Preston and C. Felcia, *The Solar System and Beyond is Awash in Water*, 2015.

3 M. Abu-Zeid, *Water Policy*, 1998, **1**, 9–19.

4 I. A. Shiklomanov, *Water Int.*, 2000, **25**, 11–32.

5 UN, *coping with water scarcity - challenge of the twenty-first century*, 2007.

6 M. Falkenmark and G. Lindh, *Water for a starving world*, Westview Press, 1976.

7 Q. Schiermeier, *Nature*, 2008, **452**, 260–1.

8 European Commision, *Report on critical raw materials for the EU*, 2010.

9 J. Cui and L. Zhang, *J. Hazard. Mater.*, 2008, **158**, 228–56.

10 M. Karvelas, A. Katsoyiannis and C. Samara, *Chemosphere*, 2003, **53**, 1201–1210.

11 B. Bergbäck, K. Johansson and U. Mohlander, *Water, Air Soil Pollut. Focus*, **1**, 3–24.

12 R. Semiat, *Water Int.*, 2000, **25**, 54–65.

13 L. Henthorne, T. Pankratz and S. Murphy, in *Desalination: Sustainable solutions for a thirsty planet*, 2011, p. 6.

14 M. A. Darwish, F. M. Al Awadhi and M. Y. Abdul Raheem, *Desalin. Water Treat.*, 2010, **22**, 193–203.

15 A. H. Galama, in *Ion exchange membranes in seawater applications : processes and characteristics*, Wageningen University, Wageningen, 2015, p. 272.

16 A. Ophir and F. Lokiec, *Desalination*, 2005, **182**, 187–198.

17 M. Al-Sahali and H. Ettouney, *Desalination*, 2007, **214**, 227–240.

18 L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot and P. Moulin, *Water Res.*, 2009, **43**, 2317–48.

19 L. Malaeb and G. M. Ayoub, *Desalination*, 2011, **267**, 1–8.

20 C. Fritzmann, J. Löwenberg, T. Wintgens and T. Melin, *Desalination*, 2007, **216**, 1–76.

21 V. A. Shaposhnik and K. Kesore, *J. Memb. Sci.*, 1997, **136**, 35–39.

22 R. Audinos, *Chem. Eng. Technol.*, 1997, **20**, 247–258.

23 T. Xu and C. Huang, *AIChE J.*, 2008, **54**, 3147–3159.

24 H. Strathmann, *Ion-Exchange Membrane Separation Processes*, Elsevier B.V., Amsterdam, 9th edn., 2001.

25 A. H. Galama, J. W. Post, M. A. Cohen Stuart and P. M. Biesheuvel, *J. Memb. Sci.*, 2013, **442**, 131–139.

26 S.-Y. Kang, J.-U. Lee, S.-H. Moon and K.-W. Kim, *Chemosphere*, 2004, **56**, 141–7.

27 F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407–418.

28 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

29 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73–80.

30 K. . Marsh, J. . Boxall and R. Lichtenthaler, *Fluid Phase Equilib.*, 2004, **219**, 93–98.

31 D. M. Fox, W. H. Awad, J. W. Gilman, P. H. Maupin, H. C. De Long and P. C. Trulove, *Green Chem.*, 2003, **5**, 724–727.

32 B. Chan, N. Chang and M. Grimmett, *Aust. J. Chem.*, 1977, **30**, 2005–2013.

33 C. Maton, N. De Vos and C. V Stevens, *Chem. Soc. Rev.*, 2013, **42**, 5963–77.

34 J. L. Anderson and D. W. Armstrong, *Anal. Chem.*, 2003, **75**, 4851–4858.

35 D. Coleman and N. Gathergood, *Chem. Soc. Rev.*, 2010, **39**, 600–37.

36 T. P. T. Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–72.

37 M. Petkovic, J. L. Ferguson, H. Q. N. Gunaratne, R. Ferreira, M. C. Leitão, K. R. Seddon, L. P. N. Rebelo and C. S. Pereira, *Green Chem.*, 2010, **12**, 643.

38 M. D. Joshi and J. L. Anderson, *RSC Adv.*, 2012, **2**, 5470.

39 M. Althuluth, M. T. Mota-Martinez, A. Berrouk, M. C. Kroon and C. J. Peters, *J. Supercrit. Fluids*, 2014, **90**, 65–72.

40 G. E. Romanos, L. F. Zubeir, V. Likodimos, P. Falaras, M. C. Kroon, B. Iliev, G. Adamova and T. J. S. Schubert, *J. Phys. Chem. B*, 2013, **117**, 12234–51.

41 M. Abai, M. P. Atkins, A. Hassan, J. D. Holbrey, Y. Kuah, P. Nockemann, A. A. Oliferenko, N. V Plechkova, S. Rafeen, A. A. Rahman, R. Ramli, S. M. Shariff, K. R. Seddon, G. Srinivasan and Y. Zou, *Dalton Trans.*, 2015, **44**, 8617–24.

42 M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–9.

43 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.

44 P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978–20992.

45 T. Vander Hoogerstraete and K. Binnemans, *Green Chem.*, 2014, **16**, 1594–1606.

46 J. G. Huddleston and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.

47 H. Zhao, S. Xia and P. Ma, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1089–1096.
48 A. E. Visser, R. P. Swatloski, S. T. Griffin, D. H. Hartman and R. D. Rogers, *Sep. Sci. Technol.*, 2001, **36**, 785–804.
49 M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124–2125.
50 A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff and A. Wierzbicki, *Chem. Commun.*, 2001, 135–136.
51 D. S. Flett, *J. Organomet. Chem.*, 2005, **690**, 2426–2438.
52 M. . Jha, V. Kumar and R. . Singh, *Resour. Conserv. Recycl.*, 2001, **33**, 1–22.
53 L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water Res.*, 2011, **45**, 4601–4614.
54 J. F. Brennecke and E. J. Maginn, *AIChE J.*, 2001, **47**, 2384–2389.
55 S. Wellens, R. Goovaerts, C. Moeller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.
56 B. Weyershausen and K. Lehmann, *Green Chem.*, 2005, **7**, 15.
57 G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacha, T. Röder and H. Sixta, *Lenzinger Berichte*, 2005, **84**, 71–85.
58 H. Zhao, *Chem. Eng. Commun.*, 2006, **193**, 1660–1677.
59 D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 2150–2163.
60 D. Dupont and K. Binnemans, *Green Chem.*, 2015, **17**, 856–868.
61 J. R. Harjani, T. Friščić, L. R. MacGillivray and R. D. Singer, *Dalt. Trans.*, 2008, 4595.
62 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.
63 X. Sun, Y. Ji, F. Hu, B. He, J. Chen and D. Li, *Talanta*, 2010, **81**, 1877–83.
64 A. Rout and K. Binnemans, *Dalt. Trans.*, 2014, **43**, 1862–1872.
65 A. Rout, K. A. Venkatesan, T. G. Srinivasan and P. R. Vasudeva Rao, *Solvent Extr. ion Exch.*, 2011, **19**, 602–618.
66 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.
67 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.
68 J.-M. Lee, *Fluid Phase Equilib.*, 2012, **319**, 30–36.
69 M. Petkovic, K. R. Seddon, L. P. N. Rebelo and C. Silva Pereira, *Chem. Soc. Rev.*, 2011, **40**, 1383–403.
70 S.-K. Mikkola, A. Robciuc, J. Lokajová, A. J. Holding, M. Lämmerhofer, I. Kilpeläinen, J. M. Holopainen, A. W. T. King and S. K. Wiedmer, *Environ. Sci. Technol.*, 2015, **49**, 1870–1878.
71 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.
72 M. Regel-Rosocka and M. Wisniewski, *Hydrometallurgy*, 2011, **110**, 85–90.
73 M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young and M. P. Jensen, *Green Chem.*, 2003, **5**, 682.
74 V. A. Cocalia, J. D. Holbrey, K. E. Gutowski, N. J. Bridges and R. D. Roqers, *Tsinghua Sci. Technol.*, 2006, **11**, 188–193.
75 M. P. Jensen, J. Neuefeind, J. V Beitz, S. Skanthakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2003, **125**, 15466–73.
76 I. Billard, A. Ouadi and C. Gaillard, *Anal. Bioanal. Chem.*, 2011, **400**, 1555–1566.
77 M. Regel-rosocka and M. Wisniewski, *Appl. Ion. Liq. Sci. Technol.*, 2011, 375–398.
78 D. Kogelnig, A. Stojanovic, F. Jirsa, W. Körner, R. Krachler and B. K. Keppler, *Sep. Purif. Technol.*, 2010, **72**, 56–60.
79 M. Regel-Rosocka, *Sep. Purif. Technol.*, 2009, **66**, 19–24.
80 D. Zhang, W. Wang, Y. Deng, J. Zhang, H. Zhao and J. Chen, *Chem. Eng. J.*, 2012, **179**, 19–25.
81 X. Sun, Y. Ji, L. Zhang, J. Chen and D. Li, *J. Hazard. Mater.*, 2010, **182**, 447–52.
82 W. Wang, H. Yang, H. Cui, D. Zhang, Y. Liu and J. Chen, *Ind. Eng. Chem. Res.*, 2011, **50**, 7534–7541.
83 J. S. Preston, *Hydrometallurgy*, 1985, **14**, 171–188.
84 J. S. Preston, *Hydrometallurgy*, 1983, **11**, 105–124.
85 J. S. Preston and A. C. du Preez, *J. Chem. Technol. Biotechnol.*, 1994, **61**, 159–165.
86 F. Miller, *Talanta*, 1974, **21**, 685–703.
87 D. K. Singh, H. Singh and J. N. Mathur, *Hydrometallurgy*, 2006, **81**, 174–181.
88 C.-B. Xia, Y.-Z. Yang, X.-M. Xin and S.-X. Wang, *J. Radioanal. Nucl. Chem.*, 2008.
89 A. Cieszyńska, M. Regel-Rosocka and M. Wiśniewski, *Polish J. Chem. Technol.*, 2007, **9**, 99–101.
90 V. Gallardo, R. Navarro, I. Saucedo, M. Ávila and E. Guibal, *Sep. Sci. Technol.*, 2008, **43**, 2434–2459.
91 E. Guibal, K. C. Gavilan, P. Bunio, T. Vincent and A. Trochimczuk, *Sep. Sci. Technol.*, 2008, **43**, 2406–2433.
92 A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2010, **73**, 202–207.
93 F. G. Seeley and D. J. Crouse, *J. Chem. Eng. Data*, 1966, **11**, 424–429.

94 T. Sato and M. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 90–94.

95 T. Sato, M. Yamamoto and K. Sato, *Solvent Extr. Res. Dev. Japan*, 2005, **12**, 101–112.

96 T. Sato, M. Yamamoto and K. Adachi, *J. Min. Mater. Process. Inst. Japan*, 2005, **121**, 603–607.

97 K. Miyashita, E. Nara and T. Ota, *Biosci. Biotechnol. Biochem.*, 2014, **57**, 1638–1640.

98 R. A. Ferrari, V. da S. Oliveira and A. Scabio, *Sci. Agric.*, 2005, **62**, 291–295.

99 S. I. El Dessouky, Y. A. El-Nadi, I. M. Ahmed, E. A. Saad and J. A. Daoud, *Chem. Eng. Process. Process Intensif.*, 2008, **47**, 177–183.

100 T. Fujii, F. Moynier, P. Telouk and M. Abe, *J. Phys. Chem. A*, 2010, **114**, 2543–52.

101 M. Regel, A. M. Sastre and J. Szymanowski, *Environ. Sci. Technol.*, 2001, **35**, 630–635.

102 M. Bartkowska, M. Regel-Rosocka and J. Szymanowski, *Chem. Technol.*, 2002, **36**, 217–224.

103 P. Wasserscheid and T. Welton, *Ionic Liquids in synthesis*, Wiley Online Library, 2008.

104 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178.

Chapter 4

Changing the selectivity due to pH and chloride concentration

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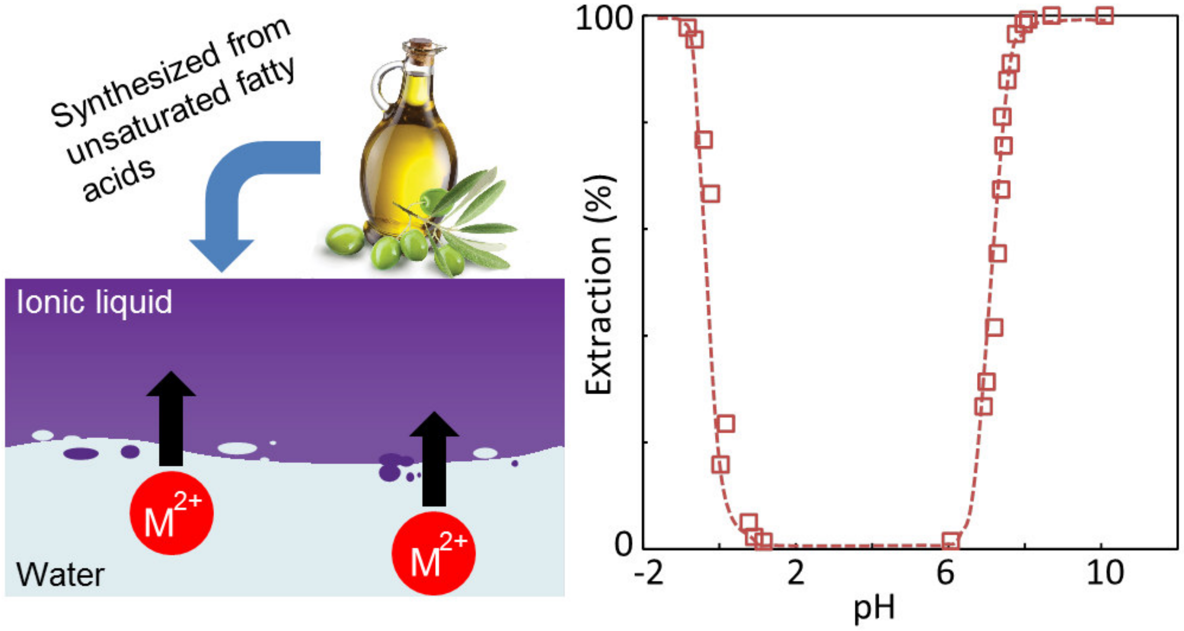

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4.1. Introduction

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 non-toxic.[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 towards 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 build into their structure. This is a metal-binding functional group in metal extraction systems.[10] In the search for biocompatible, non-toxic FILs, we recently synthesized several non-fluorinated 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 carboxylate group of the fatty acid (i.e. oleic acid) does not alter the immiscibility with water. The conjugated acids of some IL anions, such as in phthalate[12] and β-diketonates,[10c, 13] are (partly) water miscible or volatile which limits the reuse of these ILs.

Tetraoctylphosphonium oleate [P_{8888}][oleate] is a bifunctional extractant (Figure 4.1). It has the possibility to extract metals via its cation as anionic chloro complexes or via its anion by the formation of carboxylate complexes and a chloride IL ([P_{8888}][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 behaviour 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 behaviour. The aim of this paper was to investigate the effect of the HCl concentration, and consequently of 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+}, Yb^{3+} with a novel IL derived from oleic acid, i.e. tetraoctylphosphonium oleate.

4.2. Experimental

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 (≥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 delivered by GFS Chemicals. Calcium(II) chloride dihydrate and potassium chloride were delivered by VWR Chemicals as well as the sodium hydroxide pellets (99%), hydrogen chloride (37%) and absolute ethanol. The copper and gallium standard (1,000 ppm) were delivered by Chemlab. Ammonium hydroxide (35%) and oxalic acid dihydrate (>99.5%) were supplied by J.T. Baker and tetraoctylphosphonium bromide (>95%) was delivered by

IoLiTec. In addition, Milli-Q water (>18 MΩ·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 step.

Synthesis of the IL [P$_{8888}$][oleate]

The tetraoctylphosphonium oleate IL [P$_{8888}$][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 water at room temperature. Afterwards, [P$_{8888}$][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 × 200 mL) to remove NaBr, 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. ^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm): δ = 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 × C=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): Calculated for [P$_{8888}$(C$_{32}$H$_{68}$P)]$^+$ *m/z* = 483.9; found *m/z* = 483.6 and calculated for [Oleate (C$_{18}$H$_{33}$O$_2$)]$^-$ *m/z* = 281.5; found *m/z* = 281.3. Additional peaks were observed in the negative mode: 573.5 ([P$_{8888}$]$^+$ + 2 × [formate]$^-$), 809.7 ([P$_{8888}$]$^+$ + [oleate]$^-$ + [formate]$^-$), 1046.0 ([P$_{8888}$]$^+$ + 2 × [oleate]$^-$), formic acid is for 1% present in the eluens of the LC-MS.

Characterization of the IL

The purity of the IL was determined using ^{1}H and ^{13}C NMR on a 400 MHz Bruker nuclear magnetic resonance (NMR) spectrometer with and accuracy of 5%. Density and viscosity measurements of the pure IL were carried out on an Anton Paar SVM 3000/G2 type Stabinger, with an uncertainty of ± 0.0005 g/cm^3 for the density, ± 0.005 mPa·s for the viscosity, and ± 0.01 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 ± 0.01 Pa·s. Viscosities as a function of the metal loading and temperature were measured with an automatic Brookfield cone/plate viscometer/rheometer, Model LVDV-II+P CP (Brookfield Engineering Laboratories, USA), with an accuracy of ± 0.01 mPa·s. The decomposition temperature was determined with a thermogravimetric analysis (TGA) Q 500 apparatus (TA instruments, USA) at a scan rate of 10 K·min^{-1} under a nitrogen flow (see supplementary info SI 3 and SI 4). The spectra were analysed 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 1,000 ppm copper standard. Afterwards, 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-ionisation combined with mass spectrometry (ESI-MS) was used to analyse the IL after synthesis with acetonitrile as eluens. An Agilent Technologies 1200 series ESI-MS was used with acetonitrile:water 90:10 v/v as eluens working with an Agilent mass hunter workstation data acquisition.

Experimental salt extraction procedure

Various salt solutions have been prepared. A transition metal solution, containing 2,000 ppm of each metal ($MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$), a rare-earth metal solution, containing 2,000 ppm of each rare earth ($LaCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$, $ErCl_3$, $YbCl_3$), a 2,000 ppm $FeCl_3$ solution, a 2,000 ppm $InCl_3$ solution and an alkali and alkaline-earth metal solution, containing 2,000 ppm of each metal (LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$) 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 a final metal concentrations of 1,000 ppm. Metal loading of the organic phase was studied by presaturating the IL with water of the same pH as the metal solution. Afterwards, 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 4,800 ppm Ni solution and a 5,000 ppm Nd solution with 1 mL of the IL phase without adjustment of the pH. Therefore, five different mixtures were shaken at 2,000 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 concluded after investigating the kinetics of the extraction to performe all further extractions by intensive shaking at 2,000 rpm for 10 min at 40 °C, i.e. equilibrium was reached in 10 min, on a thermo shaker TMS-200 (Nemus). Later, the mixture was centrifuged on a Heraeus Labofuge 200 (Thermo Scientific) for 5 min at 5,300 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 $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $LaCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$ was analysed using a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Bruker S2 Picofox). In general, 100 µL of a gallium standard solution (1,000 ppm) was added to 100 µL of the aqueous phase and diluted until 1 mL with Milli-Q water. 20 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 analysed with TXRF. After the extraction experiments of $FeCl_3$, $InCl_3$, LiCl, NaCl, KCl, $CaCl_2$ and $MgCl_2$, the metal content of the aqueous phase was analyzed with a Perkin Elmer, 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 case of equal volumes of the aqueous and organic phase can be calculated by

$$\%E = \left(\frac{Corg}{C_{aq} + C_{org}}\right) \times 100 \qquad (1)$$

or

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

where C_{aq} and C_{org} are the metal concentrations in the aqueous phase and organic phase after extraction respectively, and $C_{aq,0}$ is the metal concentration in the initial aqueous phase. Distribution factors can be found for all the metals studied in the supplementary information.

After the extraction experiments with $NdCl_3$, the IL was regenerated by acidic stripping with an aqueous oxalic acid solution. The percentage stripped (*%S*) from the organic phase was calculated by:

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

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

$$\alpha_{Ln1,Ln2} = \frac{C_{Ln1,org}/C_{Ln1,aq}}{C_{Ln2,org}/C_{Ln2,aq}} \tag{4}$$

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 meter. 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:

$$x_i = \frac{n_i}{n_{tot}} \tag{5}$$

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

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 oxidation reactions.[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 oxidation products can influence the measured pH values in time.

4.3. Results and discussion

The influence of the pH on the metal salt extraction efficiencies of five different solutions by using the IL [P_{8888}][oleate] was investigated: (1) a transition metal solution consisting of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$, (2) a rare-earth metal solution consisting of $LaCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$, (3) an alkali and alkaline earth metal solution consisting of LiCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$, (4) a $FeCl_3$ solution, and (5) an $InCl_3$ 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.

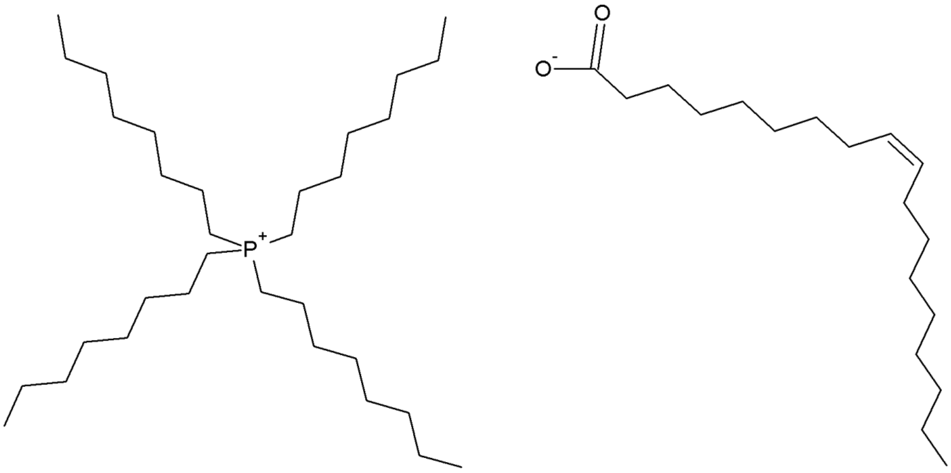


Figure 4.1. *Structure of the tetraoctylphosphonium oleate IL*

IL synthesis and characterization

In this study, the IL [P_{8888}][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 viscosity of the IL and to decrease the resistance against the mass transfer of metal ion species between the water and IL phase. Because ILs are proposed as replacements for volatile organic compounds (VOCs), it was decided to synthesize the IL [P_{8888}][oleate] without the use of VOCs. First, the synthesis of the IL was performed according to a VOCs-free synthesis reported in the literature,[35] in which the precursors, i.e. oleic acid and [P_{8888}][Br] were mixed with a 0.5 M $NaHCO_3$ solution. However, the result of 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 procedure was applied. To that end, 2 equivalents of

NaOH and 1.5 equivalents 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.

Table 4.1. *Physical properties (density, ρ; dynamic viscosity, η; kinematic viscosity, υ; melting point, T_m; decomposition temperature, T_d; bromide content, $[Br^-]$; water content, $[H_2O]$) of the IL, $[P_{8888}]$[oleate] with different water contents (wt%).*

T (K)	wt% H_2O	ρ (g/cm^3)	η (mPa·s)	υ (mm^2/s)	T_m (K)	T_d (K)	$[Br^-]$ (ppm)	$[H_2O]$ (ppm)
293 K	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 K	10.8	0.877	43.4	49.5	245.3	421.5	5	108,310
	0.49	-	900	-	-	-	5	4,900

The physical properties (melting point, decomposition temperature, density, kinematic and dynamic viscosity, water content, bromide content) of the synthesized IL $[P_{8888}]$[oleate] were measured and are collected in Table 4.1. 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 content of the IL (10.8 wt%) in comparison with the dried IL (0.49 wt%). The viscosity decreases a factor 20 at 323 K between a water content of 10.8 wt% and 0.49 wt% (Figure 4.2).

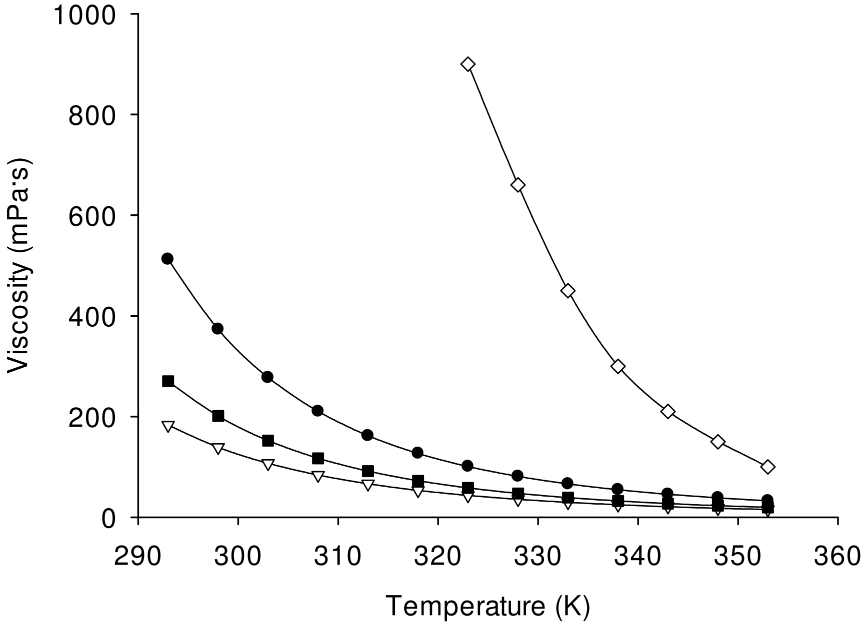


Figure 4.2. *Influence of the temperature on the viscosity of the IL [P_{8888}][oleate] with different water contents: (▽) 10.8 wt%, (■) 7.39 wt%, (●) 2.30 wt% and (◇) 0.49 wt%.*

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 as a result of an increase of the resistance against mass transfer. Nevertheless, the viscosity of an IL used in solvent extraction systems does not only depend on the cation and anion, but also on the amount of water dissolved in the IL, which is on its turn related to the structure of the IL.[20] The influence of the temperature on the viscosity of dried and water-saturated [P_{8888}][oleate] is presented in Figure 4.2. Water-saturated [P_{8888}][oleate] contains 10.8 wt% of water, which results in a rather 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 highly 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 [P_{8888}][oleate], shows that [P_{8888}][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 [P_{8888}][oleate] is comparable with the viscosity for water-saturated [C_4mim][Tf_2N] (water content 1.99 wt%, 13.3 mPa·s at 323 K) and [C_4mim][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 4.3 shows that the viscosity increased by a factor of two when it was loaded with 32,000 ppm of Nd (148 mPa·s vs. 66 mPa·s for the pure IL at 313 K), which is still significantly lower than the viscosities observed for other similar bulky metal-loaded IL extraction systems.[21] Moreover, TOC analysis showed that the solubility of [P_{8888}][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 a low viscosity, a very low water solubility and cheap starting materials makes the IL [P_{8888}][oleate] an excellent candidate for replacing organic solvents in solvent extraction studies, even on industrial scale where these kinds of properties are beneficial.

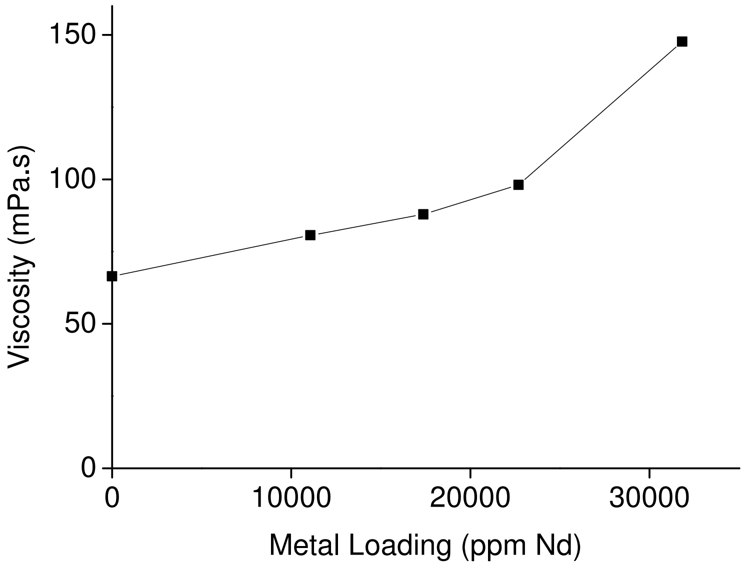


Figure 4.3. *Influence of the $NdCl_3$ loading on the viscosity of the IL [P_{8888}][oleate] at the extraction temperature of 313 K.*

It has to be reported that in this study, an ionic liquid with a non-toxic 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 limited long term stability. Especially highly acidic conditions and or metals can catalyse the degradation of the anion.[18, 19]

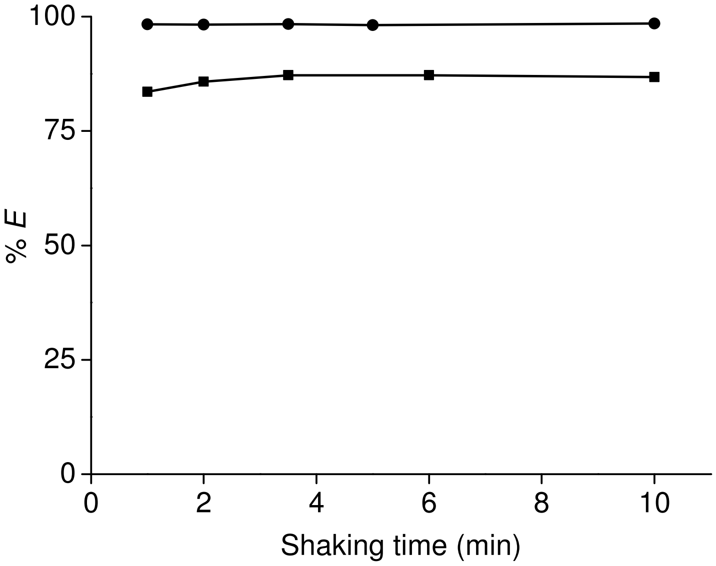


Figure 4.4. *Extraction percentage (% E) of 5,000 ppm $NdCl_3$ (●) and 4,800 ppm $NiCl_2$ (■) as a function of the shaking time.*

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 an aqueous 4,800 ppm Ni solution and an aqueous 5,000 ppm Nd solution were extracted towards 1 mL of the IL phase without adjustment of the pH. Five different mixtures were shaken at 2,000 rpm and 313 K between 1 and 10 min. Figure 4.4 shows that the Nd extraction equilibrium is already reached after 1 min with an *%E* of 98%. The equilibrium for the extraction of Ni was reached after a longer time (4 min) compared to Nd. The fast kinetics of this extraction system is most likely due to the low viscosity (66 mPa·s at 313K) of the water-saturated IL, even when the latter is loaded with metals. As shown in Figure 4.4, 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 $[P_{8888}]$[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_{8888}][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]

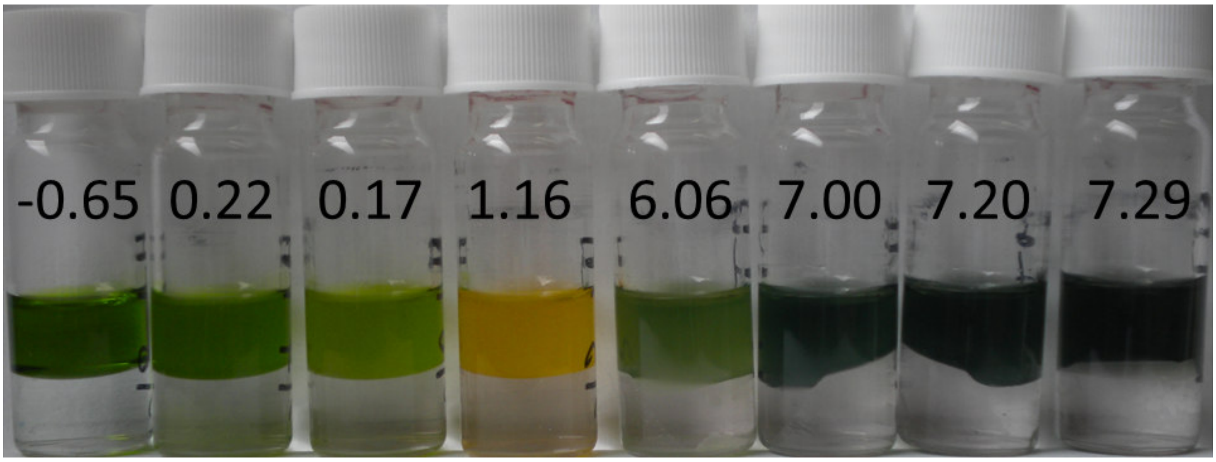


Figure 4.5. *Colour switch observed for the IL phase because of the extraction from the transition metal solution at different pH. pH of the aqueous phase is mentioned on each bottle.*

Extraction of transition metals ($MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$)

Next, extractions of a transition metal salt solution consisting of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ using [P_{8888}][oleate] were carried out at different equilibrium pH values. Figure 4.5 shows the effect of pH on the colour of the IL after extraction as a result of the different extraction behaviour. A plot showing the %*E* as a function of the pH is given in Figure 4.6. No extraction is observed for the metal ions Mn, Co and Ni at the conditions $1 \leq pH \leq 6$. The uptake of protons by the anion of the IL and the removal of the metal ions into the IL phase 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_{8888}][Cl] are formed. For consistency reasons, only pH values after extraction (equilibrium pH) are reported throughout this chapter.

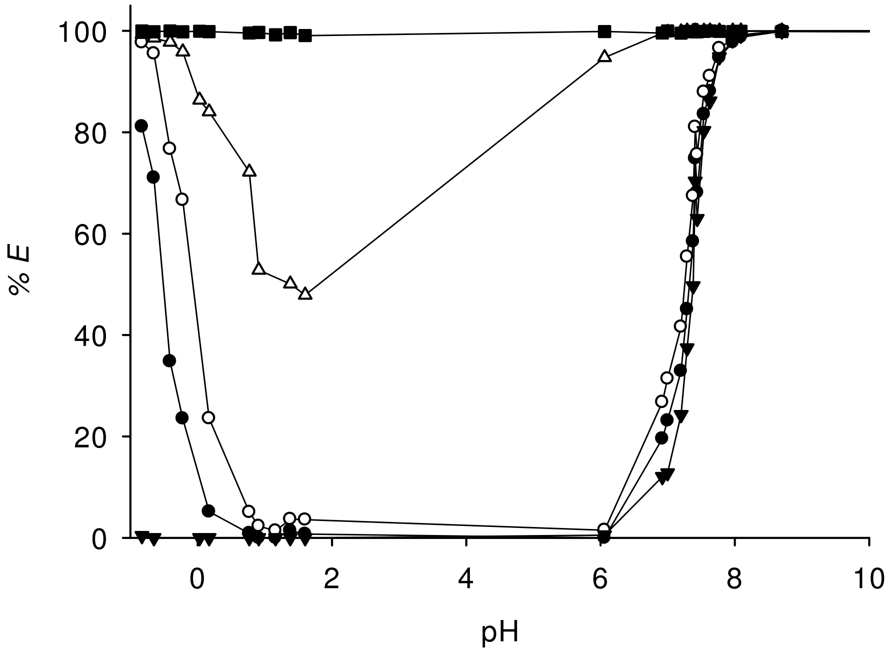


Figure 4.6. *Extraction percentage (% E) using the IL [P_{8888}][oleate] as a function of the pH for the transition metals. Zinc (■), copper (△), cobalt (○), manganese (●) and nickel (▼).*

Extraction at a pH of 7 resulted in a dark green colour of the IL because of the formation of the coloured 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 colour) between pH = 1 and pH = 6 and is not extracting metals that colour 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 4.6). 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 colouring the IL.

From Figure 4.6 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.

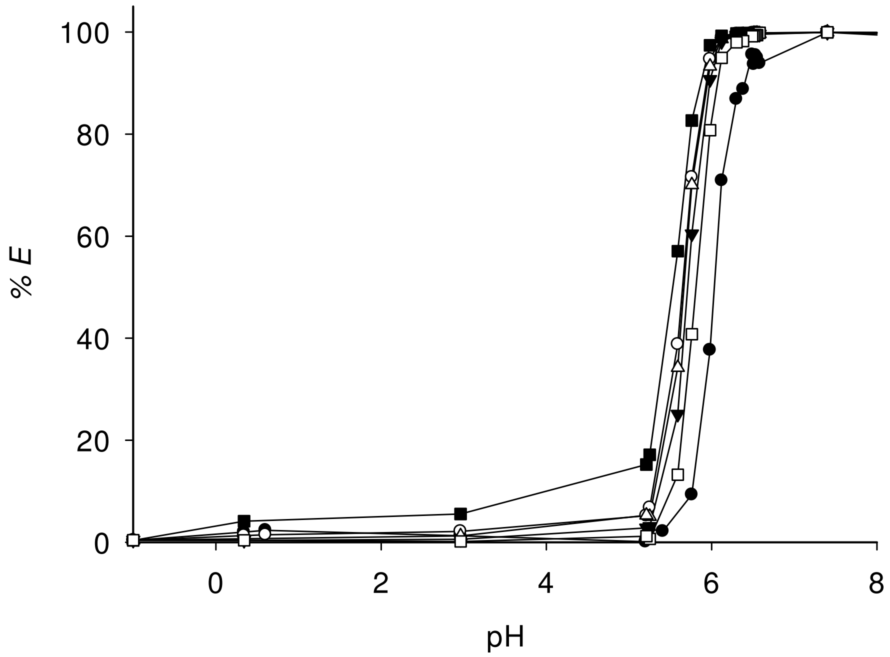


Figure 4.7. *Extraction percentage (% E) with the IL [P_{8888}][oleate] as a function of the pH for the rare-earth metals. Lanthanum (●), neodymium (□), samarium (▼), dysprosium (△), erbium (○) and ytterbium (■).*

Extraction of rare earths ($LaCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$)

Figure 4.7 shows a plot of the extraction efficiencies as a function of the pH for a rare earth solution consisting of $LaCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$. Due to low extinction coefficients for the lanthanide salts used here no colour 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 4.7 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 various 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 4.5 in the supplementary information).

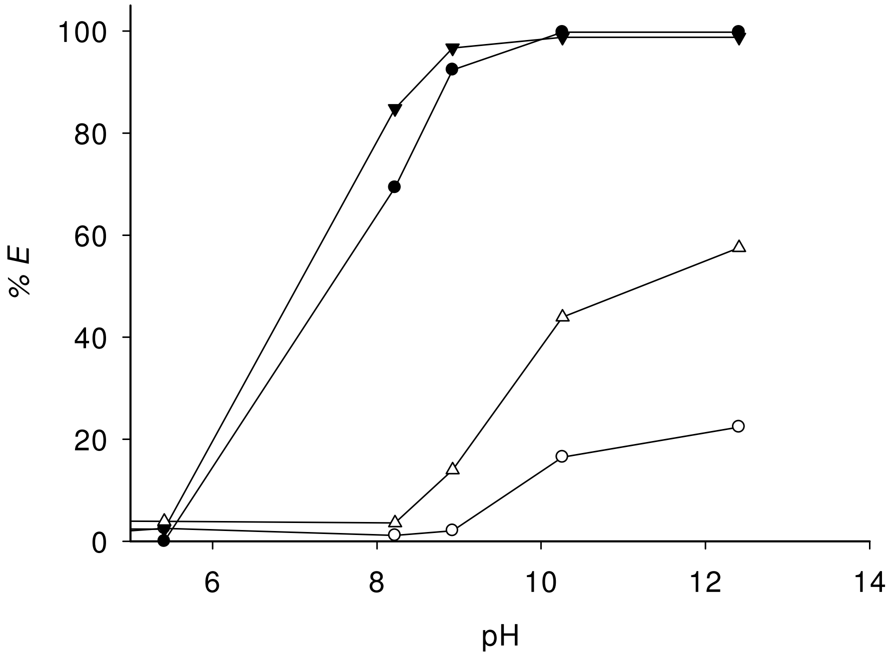


Figure 4.8. *Extraction percentage (% E) with the IL [P_{8888}][oleate] as a function of the pH for the light metals. Calcium (●), potassium (○), magnesium (▼) and lithium (△).*

Extraction of alkali and alkaline earth metals (LiCl, KCl, $MgCl_2$ and $CaCl_2$)

The extraction of alkali and alkaline earth metals from an aqueous solution with LiCl, KCl, $MgCl_2$ and $CaCl_2$ using [P_{8888}][oleate] as a function of pH is shown in Figure 4.8. No extraction was observed for these metals at pH < 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 act as an emulsifier and induces the formation of a micro-heterogeneous phase. Therefore, it is advised to avoid extraction above a pH = 9.

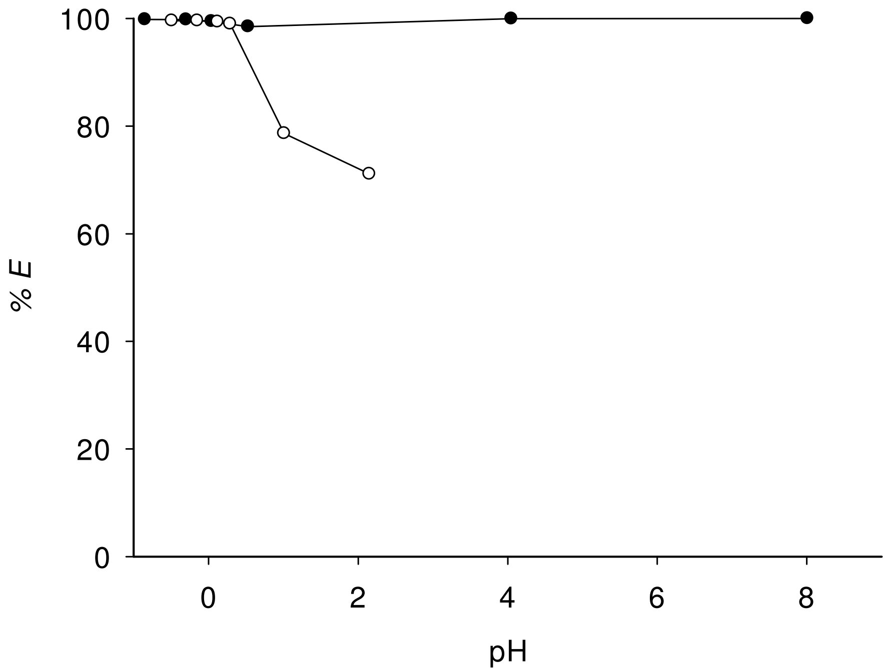


Figure 4.9. Extraction percentage (% E) with the IL [P_{8888}][oleate] as a function of the pH for $FeCl_3$ (○) and $InCl_3$ (●).

Extraction of single metal solutions ($FeCl_3$ and $InCl_3$)

The extraction of Fe(III) with [P_{8888}][oleate] is carried out separately from other metals, because it co-precipitates 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 $FeCl_3$ is shown in Figure 4.9. 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, i.e. $FeCl_4^-$.[31] At higher pH values, the water phase starts to colour red due to the formation of water soluble iron hydroxide ($Fe(OH)^{2+}$ and $Fe(OH)_2^+$) complexes.[32] Further increase of the pH (pH > 2) results in the formation of an iron(III) hydroxide precipitate. Therefore, no results of the extraction at pH > 2 were presented. The red iron precipitate can clearly be seen at the bottom of the bottle and on the phase boundary of the IL and water at pH = 7.03 in Figure 4.10.

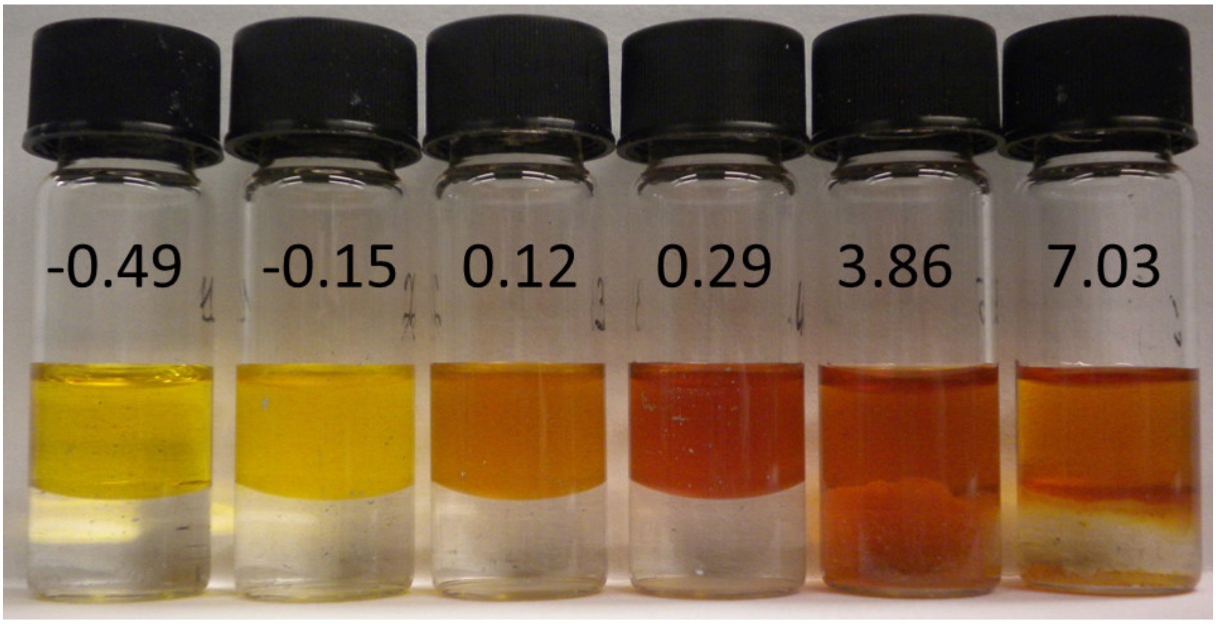


Figure 4.10. *Colour of the IL phase after extraction of $FeCl_3$ at different pH values. pH values of the aqueous phases are mentioned on each bottle.*

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 4.9 and shows that at each pH the extraction efficiency was 100%, which is similar to the extraction behaviour 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]

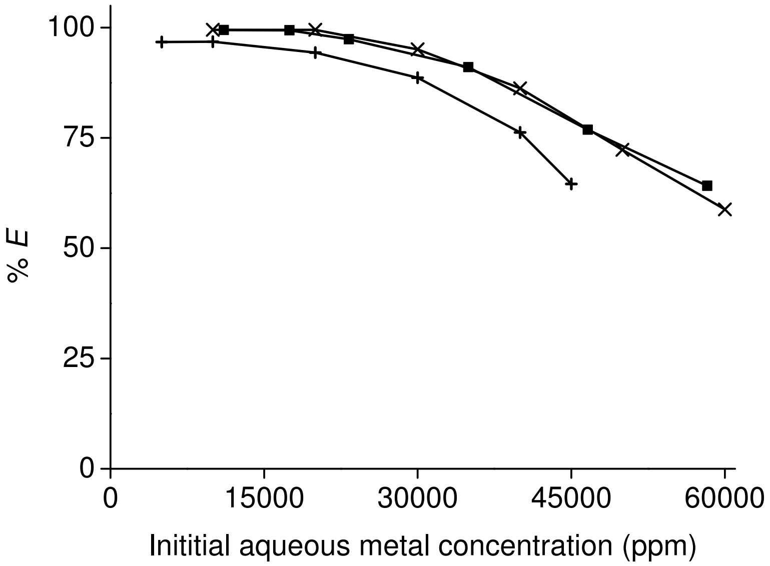


Figure 4.11. *Extraction percentage (% E) as a function of the initial aqueous La (+), Nd (■) and Yb (×) concentration.*

Metal loading of the IL

The metal loading of the IL [P_{8888}][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 4.11 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. This resulted in a decrease in extraction efficiency (Figure 4.7). 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 $Ln(OH)_3$ precipitate was observed (Ln = is a trivalent ion from the lanthanide series). This means that [P_{8888}][oleate] is not suitable for the extraction of higher rare-earth metal concentrations. The extraction efficiency of La decreased much more than that of Nd and Yb upon increasing the metal concentration in the aqueous phase. (Figure 4.11). 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 lower solubility product for $La(OH)_3$.

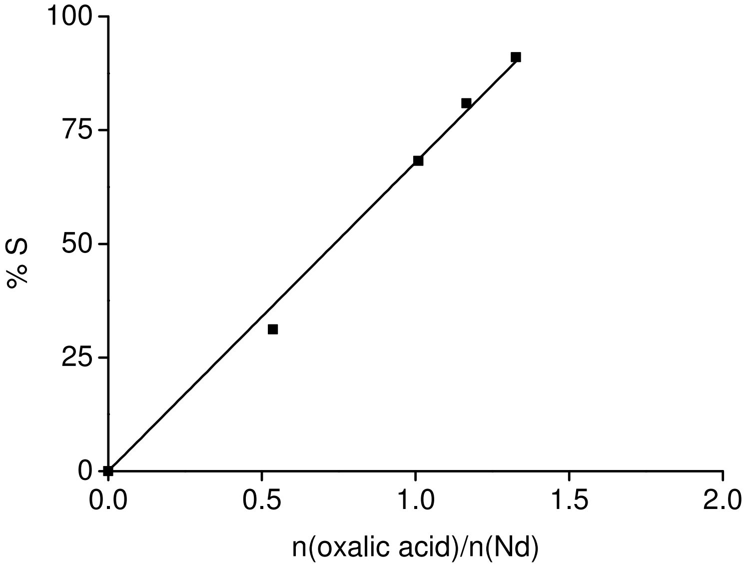


Figure 4.12. *Percentage stripped (% S) of 11,000 ppm Nd from 1 mL IL as a function of the equivalents of oxalic acid (n(oxalic acid)/n(Nd)).*

Regeneration of the IL

Because the extraction performance is strongly pH-dependent, as shown in Figure 4.7, 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 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 of Nd. (Figure 4.12). The stripping process in the case of an excess of oxalic acid can be written as:

$$2\ \overline{\mathrm{Ln(oleate)_3}} + 3\ \mathrm{H_2C_2O_4} \rightarrow \mathrm{Ln_2(C_2O_4)_3}\downarrow + 6\ \overline{\mathrm{oleic\ acid}} \quad (6)$$

It was observed that the percentage stripped metal (*%S*) increased linearly until a ratio of 1.5 moles of oxalic acid per mole of Nd (Figure 4.12). 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:

$$[\mathrm{P_{8888}}][\mathrm{oleate}] + \mathrm{H_2C_2O_4} \rightleftharpoons [\mathrm{P_{8888}}]_2[(\mathrm{C_2O_4})] + 2\ \overline{\text{oleic acid}} \qquad (7)$$

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_{8888}][Cl] are formed. 1 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. Thirdly, 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 continuously operated 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]

4.4. Conclusions

The IL tetraoctylphosphonium oleate [P_{8888}][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 rather 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_{8888}][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 of 6–7, while all rare earths are extracted from a solution with a pH of 5–6. Meaning that there is a pH difference of one unit between these metals, which shows that [P_{8888}][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, the low water solubility and a low viscosity make this IL interesting as a “green” alternative for organic solvents in industrial solvent extraction processes.

4.5. References

1 (a) C. Hagelüken, *Acta Metall. Slovaca* **2006,** *12*, 111-120; (b) K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, *J. Clean Prod.* **2013,** *51*, 1-22; (c) European Commission. *Critical raw materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials*; 2010.

2 S. Wellens, R. Goovaerts, C. Möller, J. Luyten, B. Thijs, K. Binnemans, *Green Chem.* **2013,** *15* (11), 3160-3164.

3 J. S. Wilkes, *Green Chem.* **2002,** *4* (2), 73-80.

4 M. J. Earle, J. M. S. S. Esperanca, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, J. A. Widegren, *Nature* **2006,** *439* (7078), 831-834.

5 (a) R. P. Swatloski, J. D. Holbrey, R. D. Rogers, *Green Chem.* **2003,** *5* (4), 361-363; (b) A. S. Wells, V. T. Coombe, *Org. Process Res. Dev.* **2006,** *10* (4), 794-798; (c) J. Ranke, A. Müller, U. Bottin-Weber, F. Stock, S. Stolte, J. Arning, R. Störmann, B. Jastorff, *Ecotoxicol. Environ. Saf.* **2007,** *67* (3), 430-438.

6 M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000,** *72* (7), 1391-1398.

7 (a) A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, R. D. Rogers, *Ind. Eng. Chem. Res.* **2000,** *39* (10), 3596-3604; (b) V. A. Cocalia, J. D. Holbrey, K. E. Gutowski, N. J. Bridges, R. D. Rogers, *Tsinghua Sci. Technol.* **2006,** *11* (2), 188-193; (c) J.-M. Lee, *Fluid Phase Equilib.* **2012,** *319*, 30-36.

8 M. L. Dietz, J. A. Dzielawa, *Chem. Commun.* **2001,** 2124-2125.

9 S. Chun, S. V. Dzyuba, R. A. Bartsch, *Anal. Chem.* **2001,** *73* (15), 3737-3741.

10 (a) L. Fischer, T.Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler, S. Hann, *Water research* **2011,** *45* (15), 4601-4614; (b) P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen, *Inorg. Chem.* **2008,** *47* (21), 9987-9999; (c) A. Rout, K. Venkatesan, T. Srinivasan, P. Vasudeva Rao, *Solv. Extr. Ion. Exch.* **2011,** *29* (4), 602-618; (d) H. Mehdi, K. Binnemans, K. Van Hecke, L. Van Meervelt, P. Nockemann, *Chem. Commun.* **2010,** *46* (2), 234-236; (e) J. R. Harjani, T. Friščić, L. R. MacGillivray, R. D. Singer, *Dalton T.* **2008,** (34), 4595-4601; (f) A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis Jr, R. D. Rogers, *Chem. Commun.* **2001,** (1), 135-136.

11 D. Parmentier, S. J. Metz, M. C. Kroon, *Green Chem.* **2013,** *15* (1), 205-209.

12 S. Biswas, V. Rupawate, S. Roy, M. Sahu, *J. Radioanal. Nucl. Chem.* **2014,** *300* (2), 853-858.

13 B. Onghena, J. Jacobs, L. Van Meervelt, K. Binnemans, *Dalton Trans.* **2014,** *43* (30), 11566-11578.

14 (a) W. Wang, H. Yang, H. Cui, D. Zhang, Y. Liu, J. Chen, *Ind. Eng. Chem. Res.* **2011,** *50* (12), 7534-7541; (b) V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V. Chernyshov, I. I. Torocheshnikova, S. V.Smirnova, I. V. Pletnev, *Talanta* **2010,** *80* (3), 1177-1182; (c) D. Zhang, W. Wang, Y. Deng, J. Zhang, H. Zhao, J. Chen, *Chem. Eng. J.* **2012,** *179*, 19-25; (d) X. Sun, Y. Ji, F. Hu, B. He, J. Chen, D. Li, *Talanta* **2010,** *81* (4), 1877-1883; (e) X. Sun, Y. Ji, L. Zhang, J. Chen, D. Li, *J. Hazard. Mater.* **2010,** *182* (1), 447-452.

15 (a) J. Preston, *Hydrometallurgy* **1985,** *14* (2), 171-188; (b) D. Singh, H. Singh, J. Mathur, *Hydrometallurgy* **2006,** *81* (3), 174-181.

16 (a) M. B. Bogacki, S. Zhivkova, G. Kyuchoukov, J. Szymanowski, *Ind. Eng. Chem. Res.* **2000,** *39* (3), 740-745; (b) T. Sato, T. Shimomura, S. Murakami, T. Maeda, T. Nakamura, *Hydrometallurgy* **1984,** *12* (2), 245-254.

17 (a) T. Vander Hoogerstraete, S. Jamar, S. Wellens, K. Binnemans, *Anal. Chem.* **2014,** *86* (3), 1391-1394; (b) T. Vander Hoogerstraete, S. Jamar, S.Wellens, K. Binnemans, *Anal. Chem.* **2014,** *86* (8), 3931-3938.

18 (a) K. Miyashita, E. Nara, T. Ota, *Biosci. Biotechnol. Biochem.* **1993,** *57* (10), 1638-1640; (b) R. A. Ferrari, V. d. S. Oliveira, A. Scabio, *Sci. Agric.* **2005,** *62* (3), 291-295.

19 (a) K. J. Fraser, D. R. MacFarlane, *Aust. J. Chem.* **2009,** *62* (4), 309-321; (b) S.Sowmiah, V. Srinivasadesikan, M.-C. Tseng, Y.-H. Chu, **2009,** *14* (9), 3780-3813.

20 T. Vander Hoogerstraete, B. Onghena, K. Binnemans, *Int. J. Mol. Sci.* **2013,** *14* (11), 21353-21377.

21 T. Vander Hoogerstraete, K. Binnemans, *Green Chem.* **2014,** *16* (3), 1594-1606.

22 J. Jacquemin, P. Husson, A. A. H. Padua, V. Majer, *Green Chem.* **2006,** *8* (2), 172-180.

23 (a) C. M. Neves, M. L. Batista, A. F. M. Cláudio, L. s. M. Santos, I. M. Marrucho, M. G. Freire, J. A. Coutinho, *J. Chem. Eng. Data* **2010,** *55* (11), 5065-5073; (b) M. G. Freire, P. J. Carvalho, R. L. Gardas, I. M. Marrucho, L. M. Santos, J. A. Coutinho, *J. Phys. Chem. B* **2008,** *112* (6), 1604-1610.

24 M. G. Freire, P. J. Carvalho, R. L. Gardas, L. s. M. N. B. F. Santos, I. M. Marrucho, J. o. A. P. Coutinho, *J. Chem. Eng. Data* **2008,** *53* (10), 2378-2382.

25 C. M. S. S. Neves, P. J. Carvalho, M. G. Freire, J. A. P. Coutinho, *J. Chem. Therm.* **2011,** *43* (6), 948-957.

26 H. Yu, Y.-T. Wu, Y.-Y. Jiang, Z. Zhou, Z.-B. Zhang, *New J. Chem.* **2009,** *33* (12), 2385-2390.
27 G. Georgiev, M. Zakharieva, *Monatsh. Chem.* **1989,** *120* (12), 1085-1089.
28 S. Wellens, B. Thijs, K. Binnemans, *Green Chem.* **2012,** *14* (6), 1657-1665.
29 (a) M. Sohsah. *Solvent Extr. Ion Exch.* **1990,** *8* (6), 875-892; (b) F. Seeley, D. Crouse, *J. Chem. Eng. Data* **1966,** *11* (3), 424-429.
30 J. S. Preston, *Hydrometallurgy* **1985,** *14* (2), 171-188.
31 D. Kogelnig, A. Stojanovic, F. Jirsa, W. Körner, R. Krachler, B. K. Keppler, *Sep. Purif. Technol.* **2010,** *72* (1), 56-60.
32 R. M. Cornell, U. Schwertmann, *The iron oxides: structure, properties, reactions, occurrences and uses*. John Wiley & Sons: Hoboken, 2003.
33 F. Seeley, D. Crouse, *J. Chem. Eng. Data* **1966,** *11* (3), 424-429.
34 (a) A. Glasner, M. Steinberg, *J. Inorg. Nucl. Chem.* **1961,** *22* (1), 39-48; (b) S. S. Moosath, J. Abraham, T. V. Z. Swaminathan, *Anorg. Allg. Chem.* **1963,** *324*, 90-95.
35 R. Merkl, W. Steiger, *Miner. Metall. Proc. J.* **2012,** *29* (1), 6-12.
36 A. R. Hind, S. K. Bhargava, S. C. Grocott, *Colloids Surf., A* **1999,** *146* (1–3), 359-374.

Supplementary info

S4.1. DSC scans

DSC scans were performed via a heating curve from -70 to 20 °C at 1°C·min^{-1}. Scans are obtained after subtracting the calibration line. The melting point is determined via the onset.

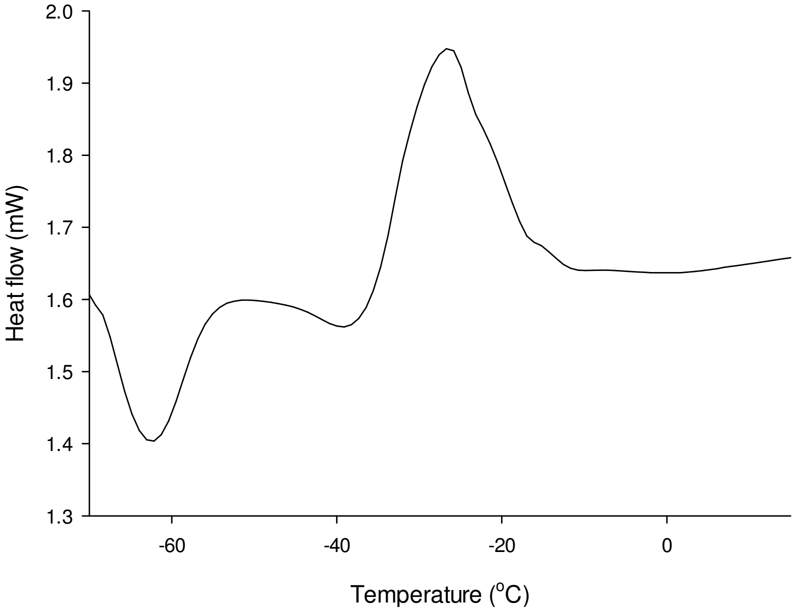


Figure S4.1. *DSC scan of the IL [P_{8888}][oleate] containing 2.3 wt% H_2O.*

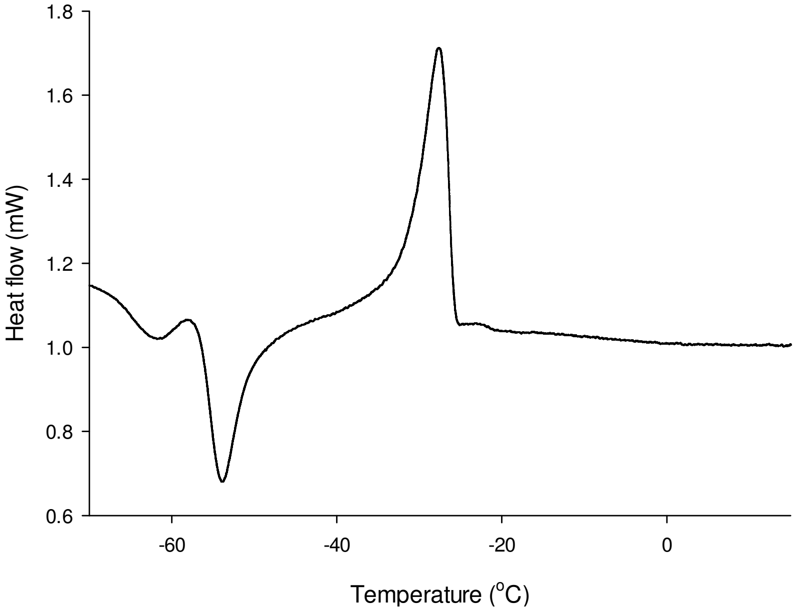
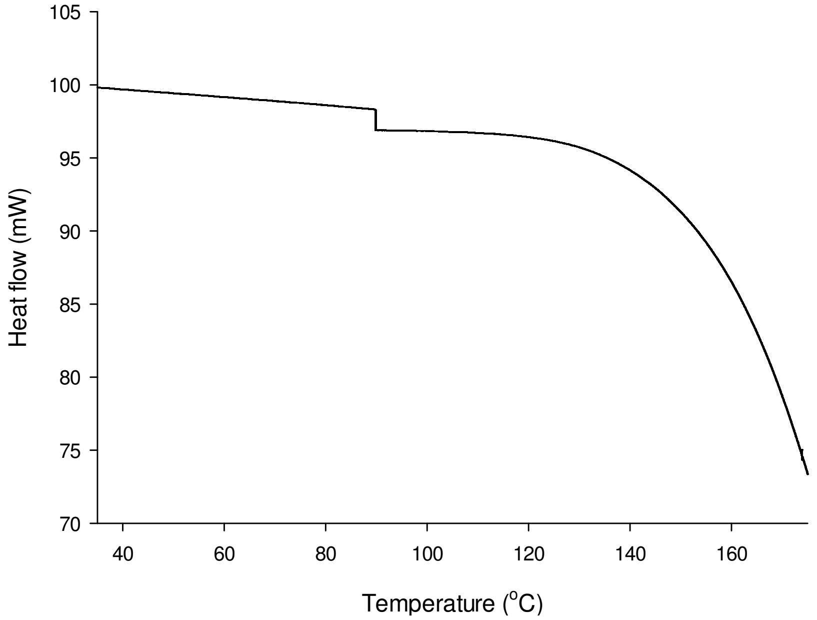


Figure S4.2. *DSC scan of the water saturated IL [P_{8888}][oleate] (10.5 wt% H_2O).*

S.4.2. TGA scans

TGA scans were first ran form 27 °C to 90 °C. Afterwards the IL was left for 2 h at 90 °C to remove the remaining water. Then, the run was continued from 90 °C to 180 °C at a heating rate of 1 °C·min^{-1}.



S4.3. *TGA scan of the dry IL [P_{8888}][oleate] (2.3 wt% H_2O).*

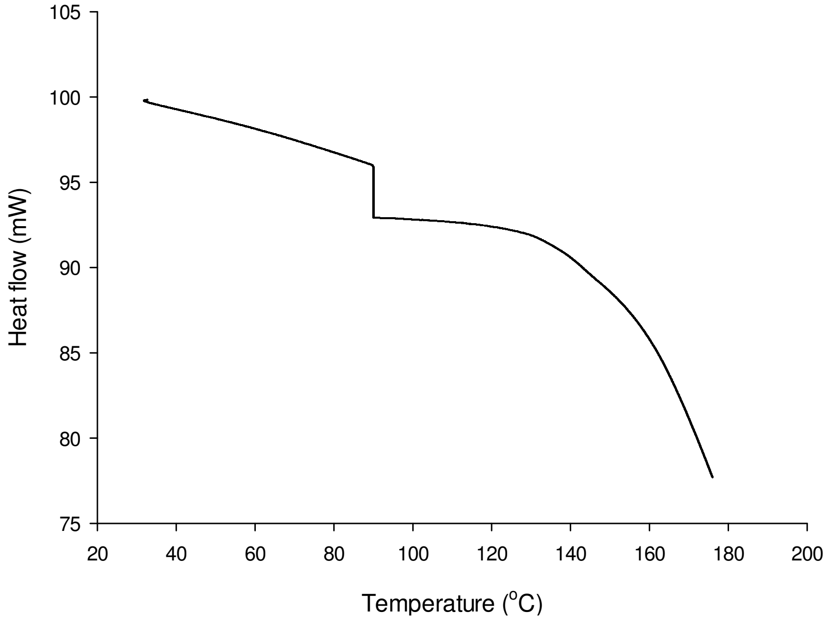


Figure S4.4. *TGA scan of the water saturated IL [P_{8888}][oleate] (10.5 wt% H_2O).*

S.4.3. Table with the separation factors of Nd, Dy, Sm, Er and Yb to La

Table S4.1. *[P_{8888}][oleate] with a solution containing 1000 ppm of La, Nd, Dy, Sm, Er, Yb.*

pH	Nd/La	Dy/La	Sm/La	Er/La	Yb/La
5.60	9	22	35	43	89

S.4.4. Picture of the oxalate precipitate obtained upon stripping of Nd from the IL

S.4.5. Distribution ratio as a function of the pH

The distribution ratio (*D*), defined in Equations (1 and 2) shows the metal concentration in the IL phase over the metal concentration in the aqueous phase. *D* was calculated for all metals extractions in function of the pH performed in this study.

$$D = \frac{C_{org}}{C_{aq}} \tag{1}$$

or

$$D = \frac{C_{aq,0} - C_{aq}}{C_{aq}} \tag{2}$$

Table S4.2. *Distribution ratio (D) as a function of the pH for zinc(II), copper(II), cobalt(II), manganese(II) and nickel(II).*

	D				
pH	Mn	Co	Ni	Cu	Zn
-0.83	4.30	43.1	0.00	151	>1000000
-0.65	2.45	21.3	0.00	70.7	636
-0.41	0.53	3.30	0.00	43.9	>1000000

-0.22	0.31	2.00	0.00	23.2	634
0.03	0.04	0.19	0.00	6.34	2610
0.17	0.05	0.31	0.00	5.28	661
0.47	9.50	0.97	0.94	1.04	24.3
0.77	0.01	0.05	0.00	2.59	235
0.91	0.00	0.02	0.00	1.12	353
1.16	0.00	0.01	0.00	0.36	132
1.38	0.01	0.04	0.00	1.00	309
1.60	0.01	0.04	0.00	0.92	108
6.06	0.00	0.02	0.01	18.0	940
6.92	0.24	0.37	0.14	243	237
7.00	0.30	0.46	0.15	363	>1000000
7.20	0.49	0.71	0.32	628	220
7.29	0.82	1.24	0.60	>1000000	1090
7.38	1.41	2.07	0.99	1250	655
7.41	2.98	4.28	2.37	>1000000	744
7.44	2.14	3.10	1.70	1270	615
7.54	5.08	7.29	4.08	2230	1370
7.63	7.39	10.2	6.21	>1000000	>10000000
7.77	18.1	28.3	18.5	>1000000	1270
7.97	43.3	63.1	54.6	>1000000	796
8.09	79.1	128	114	>1000000	1500
8.70	1350	>1000000	1870	>1000000	891

Table S.4.3. *Distribution ratio (D) as a function of the pH for the metals: lanthanum, neodymium, samarium, dysprosium, erbium and ytterbium.*

	D					
pH	La	Nd	Sm	Dy	Er	Yb
5.2	0.00	0.02	0.08	0.10	0.14	0.32
5.21	0.00	0.01	0.03	0.06	0.05	0.18
5.25	0.03	0.01	0.03	0.05	0.07	0.21
5.41	0.02	0.20	0.49	0.76	0.94	1.94
5.59	0.00	0.15	0.33	0.52	0.63	1.33

5.63	0.20	1.08	2.45	3.72	4.51	8.57
5.76	0.10	0.69	1.53	2.34	2.52	4.77
5.98	0.60	4.20	9.75	13.9	17.8	37.3
6.12	2.43	18.7	52.8	72.6	96.9	129
6.3	6.60	48.2	153	181	263	347
6.38	7.90	55.3	136	201	266	551
6.49	21.6	115	319	268	487	403
6.51	14.8	124	333	359	483	481
6.53	20.9	173	344	286	763	562
6.55	18.9	159	332	353	874	834
6.58	15.3	762	225	288	389	700

Table S.4.4. *Distribution ratio (D) as a function of the pH for calcium, potassium, magnesium and lithium*

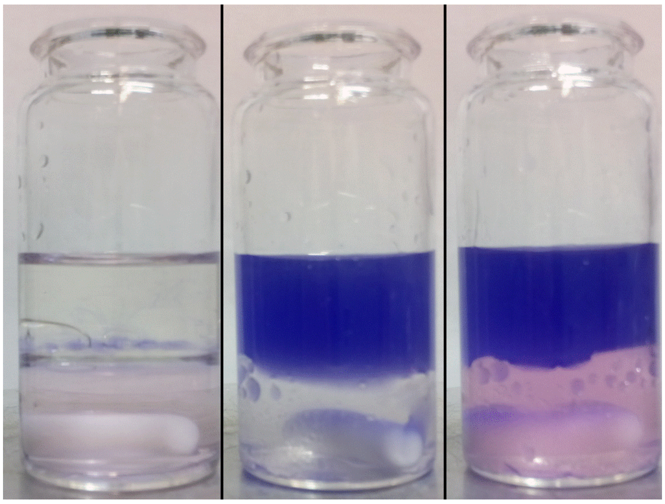
	D			
pH	Ca	K	Mg	Li
0.6	-0.10	-0.03	0.03	0.04
5.41	-0.10	0.03	0.02	0.04
8.22	2.26	0.01	5.58	0.04
8.92	12.1	0.02	29.1	0.16
10.26	415	0.20	80.8	0.78
12.41	415	0.29	80.8	1.35

Table S.4.5. *Distribution ratio (D) as a function of the pH for iron (III) and indium(III)*

pH	D_{Fe}	pH	D_{In}
-0.49	231	-0.85	544
-0.15	278	-0.3	463
0.12	174	0.04	192
0.29	103	0.53	65.0
1.01	3.68	4.05	2260
2.15	2.46	8.01	3180

Chapter 5

Regeneration of the ionic liquid



From left to right: (i) Ionic liquid (IL) in contact with the metal containing aqueous phase, (ii) IL after metal extraction (percentage extraction efficiency = 99.5%), and (iii) IL after stripping with sodium oxalate (percentage stripping efficiency = 24.3%). In all cases the IL is the upper phase.

This chapter is accepted for publication in Hydrometallurgy as:
Dries Parmentier, Yash A. Valia, Sybrand J. Metz, Odne S. Burheim and Maaike C. Kroon, Regeneration of the ionic liquid tetraoctylammonium oleate after metal extraction

5.1. Introduction

Ionic liquids (ILs) are a class of molten salts that are in the liquid phase below 100°C by definition, but mostly one refers to the room-temperature ionic liquids (RTILs), which are even liquids below room temperature. These liquids are composed of bulky organic cations in combination with organic or inorganic anions.[1] ILs recently gained a lot of interest, because they have several interesting properties, i.e. negligible vapour 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 vapour 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 demonstrated 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 or tetraalkylphosphonium cations to prevent the loss of the IL to the water phase. These hydrophobic ILs have been applied for the extraction of several transition metal ions and rare earth metal ions 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 cost-effective 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, electrodeposition is only possible when the IL has a high electrical conductivity, a low viscosity and low water uptake.[9-11] However, in some cases a higher water content is 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 ion, 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., $\mathrm{ZnCl_4^{2-}}$, $\mathrm{PdCl_4^{2-}}$, $\mathrm{ReO_4^-}$).[15-19] This usually 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 a weak acid, i.e. oxalic acid.[21-23] In this case, the metal ions form very strong water insoluble salts with oxalate that precipitate out of the IL.

Extraction of the positively charges metal ions (e.g., Ni^{2+}, Pd^{2+}, Co^{2+}) proceeds via functionalized ILs. These are ILs that contain a metal binding functionality most often in the anion,[6,24-27] but sometimes also in the cation[28-30] of the IL. Regeneration of these functionalized ILs 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.[6, 25, 29, 31-34] In most cases, these ILs cannot be directly reused for metal extraction.

The present chapter, describes the results of investigations of various options for the regeneration of the functionalized IL tetraoctylammonium oleate after metal extraction. To the best of the authors knowledge these investigations are performed for the first time. Preferably regeneration is done in a sustainable way, i.e. performed by a minimal consumption of electric energy and without the use of toxic chemicals. Detailed insights into the regeneration process will help us to evaluate how this specific IL can be applied in a continuous setup for metal extraction.

5.2. Experimental

Materials

The IL tetraoctylammonium oleate ([N_{8888}][oleate]) 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 (Meppel, The Netherlands). 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 (Zwijndrecht, Belgium). 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 (Leuven, Belgium). 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.

Electrodeposition experiments

First a test solution was made by dissolving 0.1g $CuCl_2$ in 5 mL of the pure IL [N_{8888}][oleate] (0.117 mol $Cu{\cdot}L^{-1}$ or 7.45 g $Cu{\cdot}L^{-1}$). The IL had a water content of 7.2 wt%. This concentration was used for all test solutions throughout all electrodeposition 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. The resistance of the IL was measured via a resistance meter (Agilent 4338B, Agilent Technologies), with a 0.4% relative precision.

Chemical regeneration experiments

First the IL phase was loaded with the metals of interest and used in all chemical regeneration experiments. A standard solution was prepared by dissolving a mixture of 3 salts (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}][oleate] 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 the 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 percentage extraction (*%E*) in case of equal volumes of the aqueous and organic phase can be calculated by

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

where C_{aq} stands for the metal concentrations in the aqueous phase after extraction, and $C_{aq,0}$ is the metal concentration in 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:

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

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

Cycle experiments

A cycle experiment was performed with a different 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 $Na_2C_2O_4$. 5 mL of IL and 5 mL of the start solution were applied and extraction and regeneration were performed as explained in the chemical regeneration section in a subsequent order. Extraction of these metal salts by the IL in every step of the cycle was calculated by Equation 1. Stripping efficiencies of the IL were determined by measuring the concentrations of metal salts that were remaining in the IL phase after subsequent metal extraction and stripping steps in the cycle experiment.

5.3. Results and discussion

Two different regeneration methods were tested for the reuse of the IL [N_{8888}][oleate] after metal extraction. First, electrodeposition 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 infeasible. 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 the protonation of the oleate anion to oleic acid does not alter its immiscibility with water. This is a commonly observed problem for the regeneration of ILs with conjugated acids as anions, such as in phthalate[26] and β-diketonates,[6, 35] which are (partly) transformed into water miscible or volatile chemicals during acidic stripping, so that reuse of these ILs is hampered.

Electrodeposition

When evaluating the capability of recovering metals by electrodeposition from the IL [N_{8888}][oleate] after metal extraction, $CuCl_2$ was selected as model metal salt due to the specific standard potential for copper deposition (further information in SI). First, the resistance of the IL [N_{8888}][oleate] was measured in order to obtain an indication of the conductivity. A conductivity of 0.54 $mS \cdot cm^{-1}$ was obtained for the pure IL (7.2 wt% H_2O), which is rather low compared to other commercial ILs. For example, the ILs $[EMIM]^+[C(CN)_3]^-$ and $[BMIM]^+[CF_3CO_2]^-$ have a conductivity of 18 $mS \cdot cm^{-1}$ and 3.2 $mS \cdot cm^{-1}$, respectively.[36,37] Adding $CuCl_2$ to the IL resulted only in a slight increase of the conductivity. The Cu IL test solution (0.117 mol Cu/L IL or 7.45 g Cu/L IL, 7.2 wt% H_2O) gave a conductivity of 0.91 $mS \cdot cm^{-1}$ and adding more water to this mixture until the IL mixture was water-saturated (11 wt%) increased the conductivity to 5.4 $mS \cdot cm^{-1}$. 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}][oleate] containing $CuCl_2$. After applying a potential difference of 10 V for 20 h in atmospheric conditions over the electrodes, an IL colour change from green to brown was clearly observed around the cathode. A brown layer was formed on the cathode, see Figure 5.1. 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 deposited on the electrode. This indicated that this brown layer was not due to Cu, but mainly due to a degradation product of the IL, in which some Cu^{2+} ions were enclosed.

Figure 5.1. *A brown layer could clearly be observed on the cathode (left electrode)*

It was tried to prevent the degradation of the IL by lowering the potential from 10 V to 3 V. Unfortunately, also in this case 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 Cu deposit. The fact that working in an inert atmosphere could prevent the IL from degradation indicates that oxygen is most likely reacting with the IL. Identification of the IL degradation reaction products was difficult. However, from these results, the high viscosity and high electrical resistance of the IL as well as the low IL stability (because of the many electro-active sites at the anion, i.e. the carboxyl group, the double bond and the allylic C-H bond,[38]) it was decided that metal salt recovery by electrodeposition from the IL $[N_{8888}]$[oleate] is not feasible.

Chemical regeneration

The metal ions Mn^{2+} and Co^{2+} were easily recovered from the IL by acidic stripping, because of the protonation of oleate anion and the formation of water soluble metal complexes (Table 5.1). During stripping, oleic acid is formed as well as a new IL, such as tetraoctylammonium Cl, HSO_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 for metal extraction 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, indicating that Zn forms a more stable complex with the IL compared to Mn and Co. 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]

Regeneration of the loaded IL with bases (NH_4OH and NaOH) generally results in the formation of metal precipitates. In this study, precipitates were observed in all cases where alkaline solutions were applied as stripping agents. The recoveries of metal ions from ILs using alkaline solutions as collected in Table 5.1 are expected to be lower than in reality occurring, because the stripping efficiencies were determined via analysis of the aqueous phases after stripping, whereby the precipitate formation has not been included. Zn showed the highest solubility in the aqueous stripping phase due to the excess of base, which promotes the formation of soluble $\mathrm{Zn(OH)}_4^{2-}$ or $\mathrm{Zn(NH_3)}_4^{2+}$ complexes.[39]

Table 5.1. *Regeneration of the IL by the 1.0 M H_2SO_4, CH_3CO_2H, HCl, NH_4OH and NaOH.*

%S	H_2SO_4	CH_3COOH	HCl	NH_4OH	NaOH
Co	100	92	91	20	1
Mn	100	96	100	2	1
Zn	78	52	1	78	63

Sodium salts of acids (Na_2SO_4, $NaCH_3CO_2$, $NaHCO_3$ and NaC_2O_4) were also tested as stripping agents for IL regeneration, in order to prevent protonation of oleate anion. Precipitates were also observed for all the experiments with these salts as stripping agents, which made it quantitatively difficult to mutually compare the stripping efficiency of these salts. Most voluminous precipitate was observed for the regeneration with $NaHCO_3$. Figure 5.2 presents the analysis of this precipitate with SEM. The SEM photograph shows 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 Zn from Mn and Co.

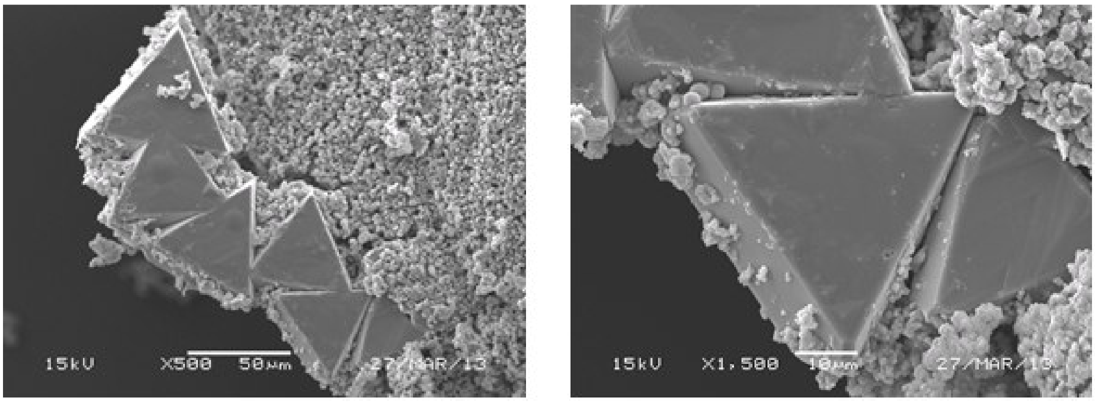


Figure 5.2. *SEM pictures of the metal carbonate precipitate shows that the triangular crystals are Zn carbonate, while granular precipitates are Mn and Co carbonate.*

From the analysis of the aqueous stripping phase, we could still get an indication of the interaction of the Na salts with the metal ions in the IL (Table 5.2). 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^{2+} and Mn^{2+} by washing with pure water, due to the weaker interaction of these metals with the IL compared to the interaction of the Zn^{2+}.

Table 5.2. *Regeneration of the IL by 1.0 M Na_2SO_4, CH_3CO_2Na, $NaHCO_3$, 0.1 M $Na_2C_2O_4$ and MilliQ water.*

%S	Na_2SO_4	CH_3CO_2Na	$NaHCO_3$	$Na_2C_2O_4$	H_2O
Co	56	30	2	82	39
Mn	84	66	2	79	71
Zn	2	1	1	68	1

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_2SO_4, CH_3CO_2Na or Milli-Q water works well to only recover the metals (Co^{2+}, Mn^{2+}) out of the IL. Alkaline solutions, like NH_4OH or NaOH, or aqueous metal extractants, like $Na_2C_2O_4$, were found to be good candidates for the regeneration of all metals from the [N_{8888}][oleate] IL.

Cycle experiments

In previous experiments precipitates were observed, preventing quantitative determination of the stripping efficiency. To minimize the occurrence of the precipitate formation, cycle experiments were conducted with single transition metal (Co) solutions using diluted NaOH (0.05 M) and $Na_2C_2O_4$ (0.1 M) as stripping solutions (Table 5.3). No precipitates were observed during the cycle experiments.

Table 5.3. *Cycle experiment showing Co^{2+} extraction efficiencies with 0.05 M NaOH (3x) and 0.1 M $Na_2C_2O_4$ (5x) as stripping solutions.*

	%E	%S	%E	%S	%E	%S	%E	%S	%E	%S
NaOH	100	1	100	0	100	0	-	-	-	-
$Na_2C_2O_4$	100	24	93	23	88	22	89	19	92	17

With 0.05 M NaOH only small stripping percentages were observed. Only three cycles were recorded, because after the third cycle a stable emulsion was observed that prevented further metal extraction. It was assumed that regenerating the IL containing Co^{2+} with NaOH resulted into the formation of an excess of sodium oleate, which is an emulsifier. Therefore, it was concluded that alkaline solutions were not feasible as stripping solutions. Additional washing steps after stripping could suppress the formation of this emulsion.

From Table 5.3 it can be concluded that $Na_2C_2O_4$ is the most promising candidate for stripping of Co^{2+} from the IL [N_{8888}][oleate]. Because long-term reuse is possible without losing extraction efficiency, this IL can be applied in a continuous metal extraction process. The metal extraction performance of the IL after regeneration by stripping stabilizes after 3 cycles at around 90%, while the stripping efficiencies remains around 20% in all cycles. Table 5.3 gives the indication that stripping efficiencies of the IL are decreasing, but one has to take into account that the stripping efficiencies were determined by measuring the concentrations of metal salts that were remaining in the IL phase after subsequent metal extraction and stripping steps in the cycle experiment.

Applying $Na_2C_2O_4$ as stripping solution results in the use of a cheap and safe chemical for regeneration by which the IL can be reused for metal extraction. The obtained metal oxalate can later on be calcined in an oven to obtain the metal oxides.[22] These metal oxides can then easily be introduced into existing metal refining processes. Contrary to other investigations on the regeneration and reuse of ILs, it was noticed that strong and weak acids are not suitable for the regeneration of this particular IL, $[N_{8888}]$[oleate]. Instead, the cheap aquatic metal extractant, $Na_2C_2O_4$, was selected as the best stripping solution.

5.4. Conclusions

Regeneration of the IL $[N_{8888}]$[oleate] by electrodeposition after metal extraction was not possible due to the high resistance and viscosity of the IL. Furthermore, degradation of the IL occurred in the presence of oxygen. Chemical regeneration made it possible to selectively strip different metals from the IL as a result of the stability of the different IL metal complexes formed. 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 forming weaker IL metal complexes. 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 agent for the regeneration of the IL $[N_{8888}]$[oleate] after metal extraction, because the IL does not lose its high extraction efficiency for Co, Mn and Zn after multiple regeneration cycles.

5.5. References

1. J. S. Wilkes, *Green Chem.*, 2002, 4, 73-80.
2. X. Sun, Y. Ji, F. Hu, B. He, J. Chen and D. Li, *Talanta*, 2010, 81, 1877-1883.
3. S. Wellens, R. Goovaerts, C. Möller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, 15, 3160-3164.
4. D. Zhang, W. Wang, Y. Deng, J. Zhang, H. Zhao and J. Chen, *Chem. Eng. J.*, 2012, 179, 19-25.
5. T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, 4, 1659-1663.
6. A. Rout, K. Venkatesan, T. Srinivasan and P. Vasudeva Rao, *Solv. Extr. Ion. Exch.*, 2011, 29, 602-618.
7. D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, 15, 205-209.
8. D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans and M. C. Kroon, *Ind. Eng. Chem. Res.*, 2015, 18, 5149–5158
9. P.-Y. Chen and Y.-T. Chang, *Electrochim. Acta*, 2012, 75, 339-346.
10. E. Abedin, S. Zein, E. Moustafa, R. Hempelmann, H. Natter and F. Endres, *Electrochem. commun.*, 2005, 7, 1111-1116.
11. F. Endres, *ChemPhysChem*, 2002, 3, 144-154.
12. A. P. Abbott and K. J. McKenzie, *Phys. Chem. Chem. Phys.*, 2006, 8, 4265-4279.
13. A. P. Abbott, G. Frisch, J. Hartley and K. S. Ryder, *Green Chem.*, 2011, 13, 471-481.
14. A. P. Abbott, J. Collins, I. Dalrymple, R. C. Harris, R. Mistry, F. Qiu, J. Scheirer and W. R. Wise, *Aust. J. Chem.*, 2009, 62, 341-347.
15. M. Regel-Rosocka and M. Wisniewski, *Hydrometallurgy*, 2011, 110, 85-90.
16. K. M. Rohal, D. M. V. Seggen, J. F. Clark, M. K. McClure, C. Kevin Chambliss, S. H. Strauss and N. C. Schroeder, *Solvent extr. and ion exc.*, 1996, 14, 401-416.
17. A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2011, 80, 385-389.
18. M. Regel-Rosocka, *Sep. Purif. Technol.*, 2009, 66, 19-24.
19. T. Vander Hoogerstraete and K. Binnemans, *Green Chem.*, 2014, 16, 1594-1606.
20. H.-L. Yang, W. Wang, H.-M. CUI and J. CHEN, *Chinese J. Anal. Chem.*, 2011, 39, 1561-1566.
21. T. Vander Hoogerstraete, B. Blanpain, T. Van Gerven and K. Binnemans, *R. Soc. Chem. Adv.*, 2014, 4, 64099-64111.
22. D. Dupont and K. Binnemans, *Green Chem.*, 2015.
23. D. Dupont and K. Binnemans, *Green Chem.*, 2015.
24. V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V. Chernyshov, I. I. Torocheshnikova, S. V. Smirnova and I. V. Pletnev, *Talanta*, 2010, 80, 1177-1182.
25. L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water research*, 2011, 45, 4601-4614.
26. S. Biswas, V. Rupawate, S. Roy and M. Sahu, *J. Radioanal. Nucl. Chem.*, 2014, 300, 853-858.
27. T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *Int. J. Mol. Sci.*, 2013, 14, 21353-21377.
28. A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis Jr and R. D. Rogers, *Chem. Commun.*, 2001, 135-136.
29. J. R. Harjani, T. Friščić, L. R. MacGillivray and R. D. Singer, *Dalton T.*, 2008, 4595-4601.
30. P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan and M. T. Nguyen, *Inorg. Chem.*, 2008, 47, 9987-9999.
31. A. Rout and K. Binnemans, *Dalton Trans.*, 2014, 43, 1862-1872.
32. J. D. Holbrey, A. E. Visser, S. K. Spear, W. M. Reichert, R. P. Swatloski, G. A. Broker and R. D. Rogers, *Green chem.*, 2003, 5, 129-135.
33. A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis Jr and R. D. Rogers, *Chem. Commun.*, 2001, 135-136.
34. A. Rout, J. Kotlarska, W. Dehaen and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, 15, 16533-16541.
35. B. Onghena, J. Jacobs, L. Van Meervelt and K. Binnemans, *Dalton Trans.*, 2014, 43, 11566-11578.
36. P. Wasserscheid and T. Welton, *Ionic liquids in synthesis*, Wiley Online Library, 2008.
37. P. Bônhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. chem.*, 1996, 35, 1168-1178.
38. H. J. Schäfer, *Eur. J. Lipid Sci. Tech.*, 2012, 114, 2-9.
39. R. A. Reichle, K. G. McCurdy and L. G. Hepler, *Can. J. Chem.*, 1975, 53, 3841-3845.

Supplementary info

S5.1. Resistance measurements

The resistance of the IL was measured via a resistance meter (Agilent 4338B, Agilent Technologies), with a 0.4% relative precision, by placing 2 Pt_{80}/Ir_{20} wires with a diameter of 0.25 mm on a distance of 1 cm from each other in the liquid. In this setup, a resistance of 34 kΩ was measured for a 0.01 M KCl standard solution, which has a standard conductivity of 1.413 $mS{\cdot}cm^{-1}$. To be able to compare our results with other data, we calculated via Equation 1 the geometry factor (G) for our cell that we used to determine the resistance:

$$G = \kappa R \qquad \text{(Eq. 1)}$$

for which κ stands for the standard conductance and R stands for the measured resistance.

From Equation 1, we can calculate that the geometry factor (*G*) of our cell corresponds to 48. All conductivities (σ) reported in this chapter are calculated via Equation 2.

$$\sigma = \frac{1}{R} G \qquad \text{(Eq. 2)}$$

A resistance of 89 kΩ was obtained for the pure IL (7.2 wt% H_2O) and from Equation 2 it was calculated that the conductivity of our pure IL corresponds to 0.54 $mS{\cdot}cm^{-1}$. Adding $CuCl_2$ to this IL resulted in a resistance of 53 kΩ or a conductivity of 0.91 $mS{\cdot}cm^{-1}$. Adding more water to this mixture until the Cu-IL mixture is fully water-saturated (11 wt%) lowered the resistance to 8.9 kΩ, resulting, resulting in an increased conducitivity of 5.4 $mS{\cdot}cm^{-1}$.

When evaluating the capability of recovering metals by electrodeposition from the IL $[N_{8888}]$[oleate] after metal extraction, $CuCl_2$ was selected as model metal salt due to the specific standard potential for copper deposition. That is, electrodeposition 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, a model metal salt was selected that not competed 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 the reaction $2H^+ + 2e^- \rightarrow H_2$).

When considering water, there are two phenomena that could favor the hydrogen cation reduction (hydrogen gas 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 decreases, 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 decreased by 30 mV (2.303*RT/2F). For the hydrogen cation reduction (hydrogen gas 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 unit). In all instances the pH of the solutions were indicated to be well above 7, which means that the copper will always be favoured when evaluating the reversible potentials. The other phenomenon that would favour 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, the Cu^{2+} ion will either not access the cathode or it could be impeded from diffusing or migrating to the 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 that of H^+. Since the former of the two phenomena would never occur, the latter would demonstrate limitations currently effective for the IL [N_{8888}][oleate]. Pinpointing challenges as such is important in developing adequate ILs and therefore an important aspect of this paper.

S5.2. SEM and EDX analysis of the metallic deposit

Procedure: The (Co, Mn, Zn)CO_3 precipitate was obtained by decantation of the aqueous phase after stripping the metal (Co, Mn, Zn) containing IL with $NaHCO_3$. Afterwards the precipitate was dried in a vacuum oven. Before analyzing the precipitate by SEM, a gold layer was sputtered on top of the sample via a JEOL-sputter coater. Afterwards, the sample was inserted into the JSM-6480LV scanning electron microscope (SEM) for imaging. Element analysis was then performed via an energy dispersive X-ray analysis (EDXA) of NORAN.

Result: From the results of the EDX analysis (Figure S5.2 and Table S5.1) of the triangular crystals observed in Figure 5.1, it could be concluded that the triangular crystals were composed of $Zn(HCO_3)_2$. On the other hand, Figure S5.3 and Table S5.2 show the results of the EDX analysis for the granular precipitate observed in Figure S5.1. The results in Figure S5.3 en Table S5.2 show that the metals Mn, Co and Zn are present in the granular precipitate. This was all verified by the EDX analysis of the cross section shown on Figures S5.4 and S5.5.

SEM and EDX analysis of the triangular crystals

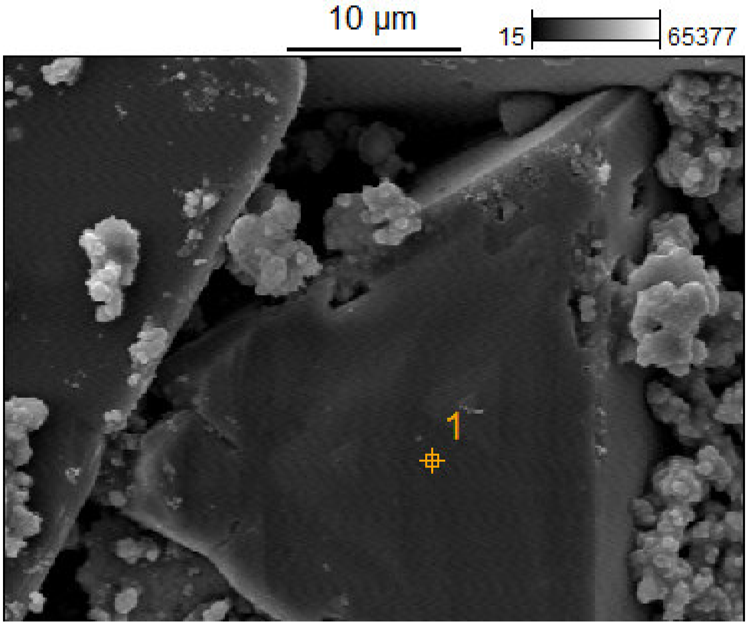


Figure S5.1. *Image of the triangular crystals observed in the precipitate after applying $NaHCO_3$ as stripping solution. Magnification of the image: 2700, image resolution: 512 by 392, image pixel size: 0.08 µm, acceleration voltage: 15.0 kV.*

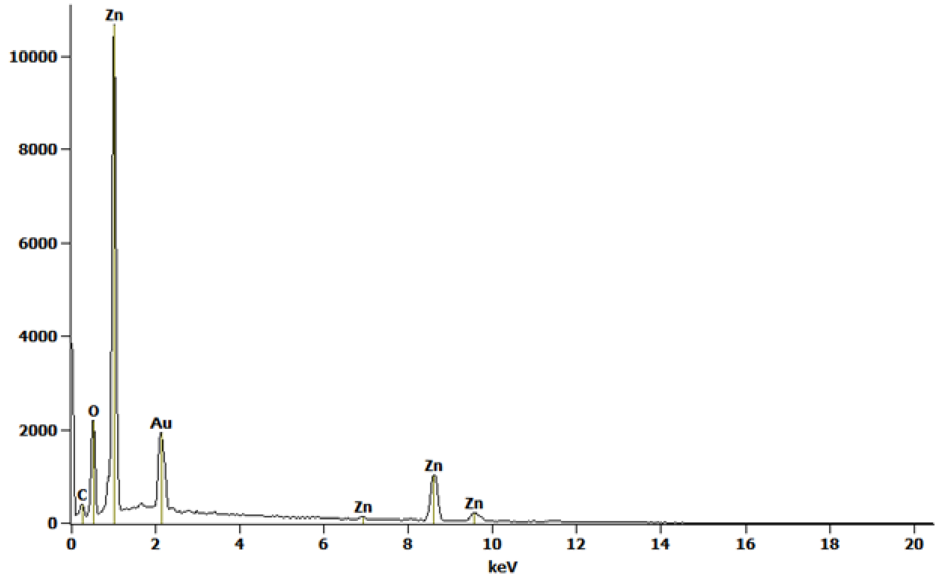


Figure S5.2. *EDX analysis of the triangular crystals measured at position 1 in Figure S5.1.*

Table S5.1. *Weight and atom percentage of the triangular crystals calculated from Figure S5.2.*

Element Line	Weight %	Atom %
C K	3.78	10.43
O K	29.25	60.62
Zn K	52.18	26.46
Au M	14.79	2.49
Total	100.00	100.00

EDX analysis of the granular crystals

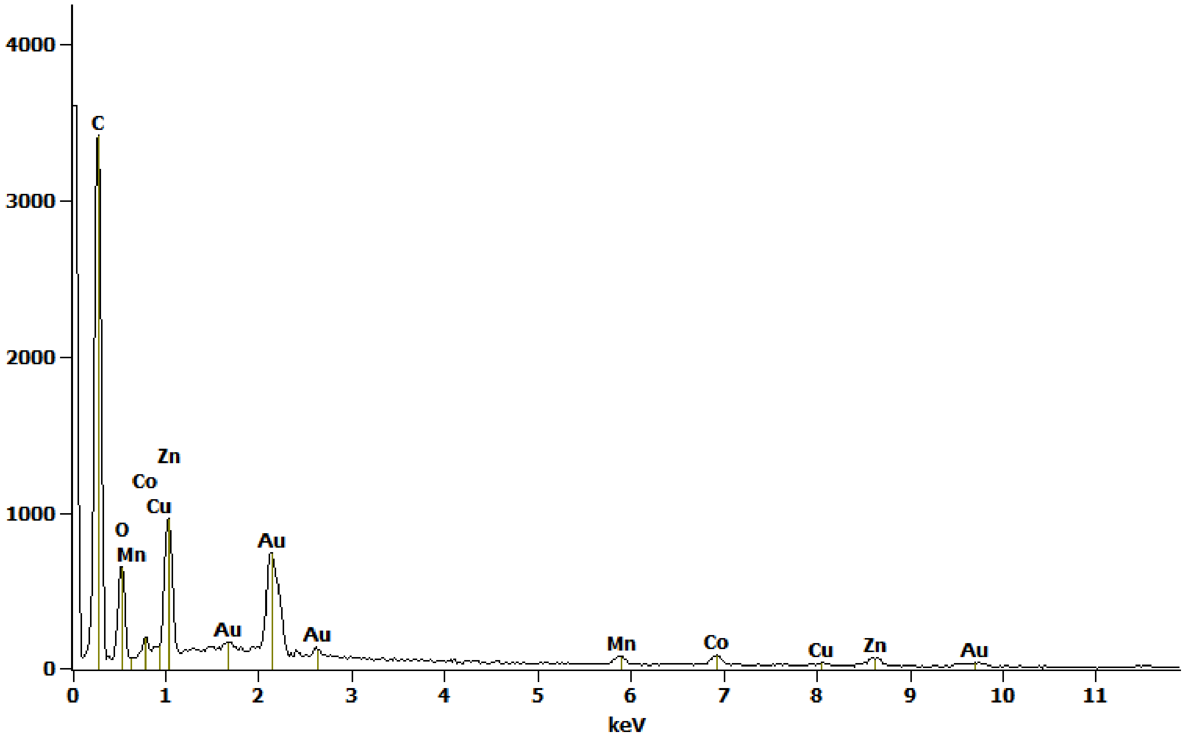


Figure S5.3. *EDX analysis of the granular precipitate that can be observed in Figure S5.1. Measured with a magnification of a factor 10000.*

Table S5.2. *Weight and atom percentage of the triangular crystals calculated from Figure S5.3.*

Element Line	Weight %	Atom %
C K	49.95	49.95
O K	27.36	27.36
Mn K	1.64	1.64
Co K	2.70	2.70
Cu K	1.58	1.58
Zn K	6.80	6.80
Au M	9.96	9.96
Total	100.00	100.00

SEM and EDX analysis of a cross section over the (Na, Co, Mn, Zn, H) CO_3 precipitate.

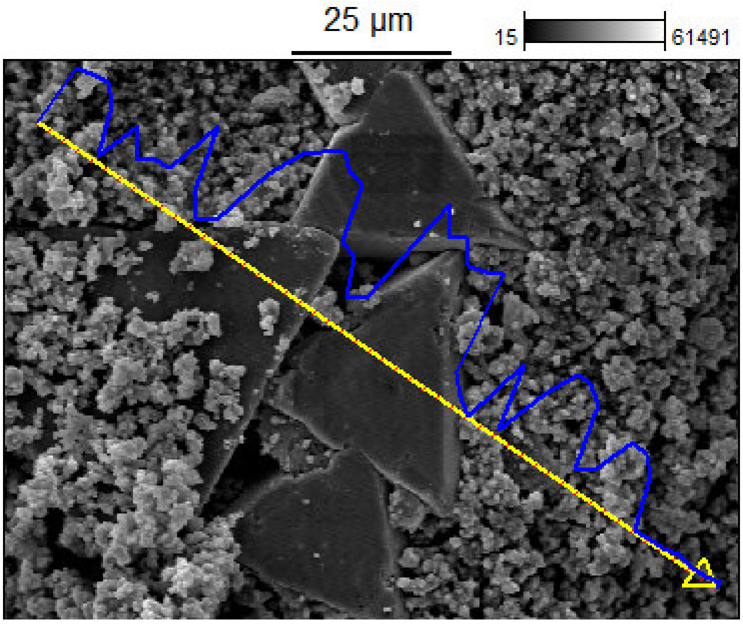


Figure S5.4. *SEM image on which is represented with a yellow line the cross section on which and EDX analysis was perfomed over the precipitate. The blue line represents the amount of counts that were detected for zinc over this cross-section. Magnification of the image: 1000, accelerating voltage: 15.0 kV.*

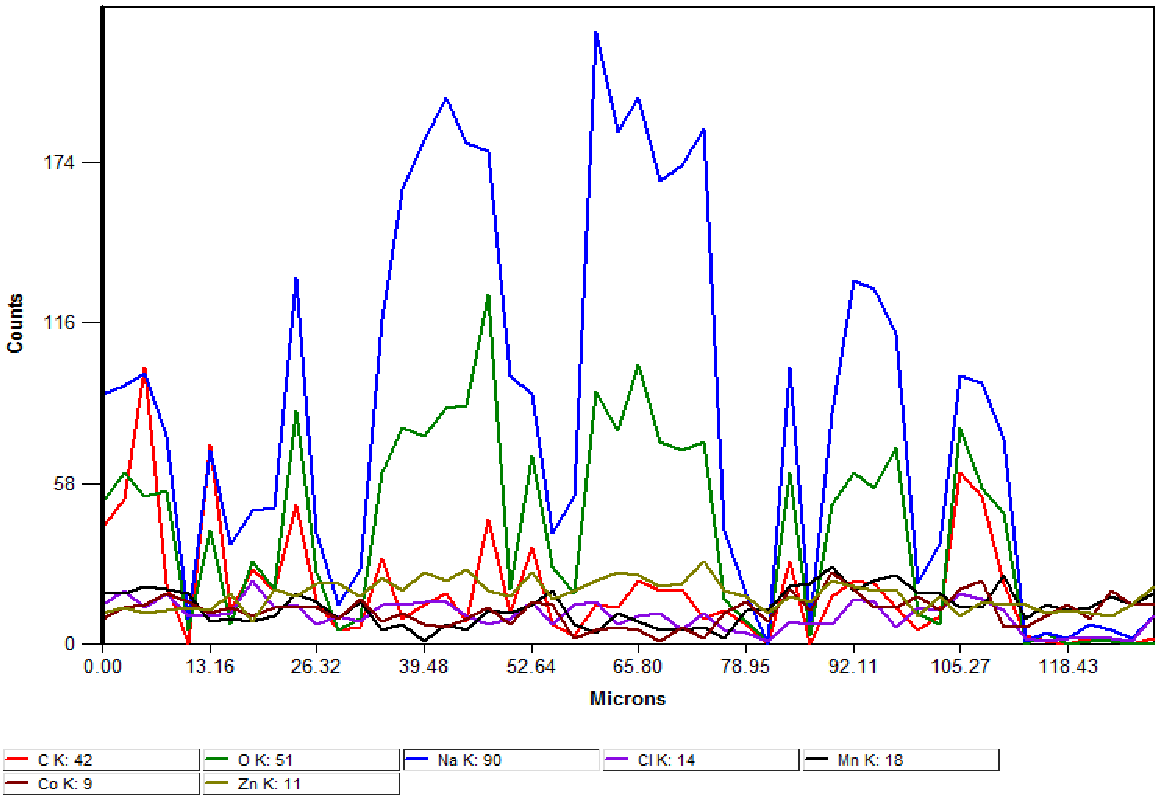
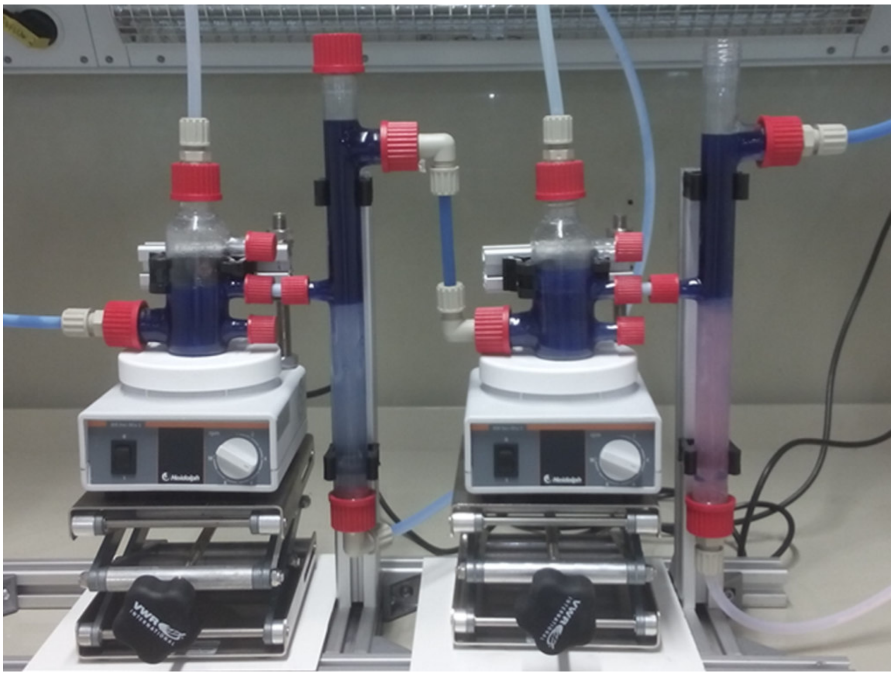


Figure S5.5. *EDX analysis of the cross section over the precipitate observed in Figure S5.4.*

Chapter 6

Continuous process for selective metal extraction



This chapter is submitted to Chemical Engineering Journal as:
Dries Parmentier, Sara P. Vilar, Sybrand J. Metz, Susanne K. Wiedmer and Maaike C. Kroon, Continuous setup for selective metal extraction with the ionic liquid tetraoctylphosphonium oleate.

6.1. Introduction

Despite the vast amount of water on the Earth, less than 1% of this water is readily available for our use as freshwater.[1] To make matters more complicated, humanity already consumes more than 50% of this available water, while there are still billions of people that lack the most basic water services.[2] The areas suffering from water scarcity are increasing, and this is mostly due to exhaustion and prolonged periods of low rainfall or drought. The effects of this water scarcity are diverse: reduced river flows, lowered lake and groundwater levels, drying up of wetlands, desertification, et cetera. The growing crisis of water scarcity is also accompanied with a water quality crisis. Where the water resource has diminished, a worsening of water quality has normally followed, because there is less water to dilute pollutants.[3] The problems related to water quality and quantity have led to an increasing need of devising sustainable techniques of water purification, allowing for its posterior reuse.

Water pollution caused by the presence of heavy metals, which can be found naturally in water sources or caused by unregulated urbanization and industrialization, has become of global concern due to its toxicity to human beings and ecosystems.[4] Metals are not biodegradable and can thus easily bio-accumulate and bio-magnify in trophic chains. This has led to a profound study of the health implications of each metal to establish permissible metal concentrations in drinking water.[5] On the other hand, metals are valuable for industrial purposes, and the European Commission has identified 14 metals with a high industrial demand, but limited production sources.[6] Therefore, metal extraction and recovery should both be taken into account in the same process to reduce health risks, and to recover valuable raw materials.

There are diverse techniques available for metal recovery. Traditionally, solvent extraction was one of the major hydrometallurgical techniques for metal separation and recovery.[7] The extraction phase is composed of organic solvents, which contain compounds with high affinity for metal ions, such as organophosphorus acids,[8] ketones,[9] amines[10] and carboxylic acids.[11] However, solvent extraction requires the use of large amounts of volatile organic solvents, which are toxic for the environment.[12,13] Chemical precipitation is another metal recovery method, which has promising qualities as it is relatively simple and inexpensive to operate, but it also has its limitations, e.g. it may not be effective in the presence of complexing agents, sulphide precipitation may release toxic fumes of H_2S in time, and sludge disposal is complicated. Furthermore, precipitation is only effective at high metal concentrations, whereas wastewater usually contains very low concentrations of metals.[14–16] Ion-exchange columns are currently the most applied technique for metal recovery: they have high removal efficiencies, high exchange rates and can selectively remove metals.[17] However, its mechanism consists of exchanging an ion, which is then discharged. This ion is often a proton, which can change the pH of the discharged water, or sodium, which can lead to brackish water. Additionally, these resins need to be regenerated using strong acids or bases, and recovery of metals from the produced brine solution for its posterior use is more difficult.[14] Bio-sorption, another metal removal technique, does not use toxic leachates or expensive absorbents. However, it is hard to obtain efficient recoveries due to the unpredictable behaviour of microorganisms in the presence of other metals.[13] Recovery of the metals for their posterior use is also complicated. Concerning membrane filtration (ultrafiltration, reverse osmosis, nanofiltration, and electrodialysis), the removal of metals from water is efficient, but these metal recovery techniques are expensive, require restoration of membranes (possible bio-fouling and/or scaling) and there is a lack of selective metal recovery.[14,16]

Due to ever-increasing concerns for sustainable practices, novel techniques need to be designed. These should be economic, so that their use can be spread to developing countries, as these countries have the most metal-contaminated aquifers.[4,18] They should also have a low energy consumption, which makes electrodeposition unfeasible as suitable recovery technique. Finally, the materials used in the process should be non-toxic. Based on these criteria, a newly synthesized ionic liquid (IL), tetraoctylphosphonium oleate ([P_{8888}][oleate]), was chosen, which shows promising characteristics as extractant for sustainable selective metal recovery.[19]

ILs are ionic salts which are liquids at room temperature, and are also referred to as “molten salts”.[20] The ions in these liquids are large and are held together by electrostatic attractions, which result in different physical and chemical properties compared to conventional solvents. They are liquid over a wide range of temperatures and have a negligible vapour pressure.[21] Selecting specific anions and/or cations leads to ILs which can have high extraction efficiencies for metals.[22–25]

In this work, a fatty acid based IL that shows excellent extraction efficiencies for transition metal ions and rare earth metal ions, was applied.[26] Moreover, the selectivity of [P_{8888}][oleate] towards the extracted metal ions can be adjusted by changing the pH and chloride concentration.[26] Due to the very high metal affinity of the IL, even trace amounts of metals can be extracted, which is useful for trace amounts of toxic or valuable metals found in anthropogenic or natural polluted water.[4,18]

However, ILs are still expensive compared to conventional solvents and extractants. Therefore, regeneration and reuse of the IL is important. Regeneration also has to be done in a sustainable manner (minimizing the use of chemicals and energy) and should not generate additional waste. For this purpose we applied an aqueous 0.1 M sodium oxalate solution as stripping agent to recover the metals.[27]

For the first time a small demo of a continuous process was built in order to test the continuous selective extraction capacity of the IL [P_{8888}][oleate]. In this process, selective metal extraction of an aqueous waste stream was done in one compartment, while in a second compartment the IL loaded with a metal was stripped so that the IL can be recirculated to be reused for metal extraction. Only one other paper on continuous metal separation, using another type of IL, was found in literature,[28] but in that work the extraction was operated with different salt mixtures (Co/Ni) in five mixer-settlers at 50 °C instead of two mixer-settlers at room temperature. In this study, we will also evaluate the long-term stability, degradation and harmfulness of the IL, as well as the cost effectiveness of the continuous process.

6.2. Experimental

Materials

Tetraoctylphosphonium bromide (>95%) was supplied by Iolitec (Heilbronn, Germany). Oleic acid (90%) and sodium oxalate dihydrate (98%) were delivered by Alfa Aeser (Karlsruhe, Germany). Cobalt(II) chloride hexahydrate (99%) and monobasic hydrogen sodium phosphate (≥99.0%) were delivered by Sigma-Aldrich (Zwijndrecht, Belgium). Sodium hydroxide (≥97%), calcium chloride dihydrate (≥99%) and potassium chloride (≥99%) were delivered by VWR Chemicals (Leuven, Belgium). Chloroform (>99%) was purchased from Rathburn Chemicals Ltd. (Walkerburn, UK). 1-Palmitoyl-2-oleyl-*sn*-glycero-3-[phospho-rac-(1-glycerol)] (sodium salt) (POPG) was purchased from Genzyme Pharmaceuticals (Liestal, Switzerland) and L-α-phosphatidylcholine (Egg, Chicken) (EggPC) was from Avanti Lipids (Alabaster, AL, USA). MilliQ water (≥18.2 MΩ·cm) used throughout the synthesis and extraction/regeneration experiments utilized and was obtained by a Millipore MilliQ® biocel, which used a Q-grade® column.

Synthesis of the ionic liquid [P_{8888}][oleate]

For this research the IL was synthesized on a larger scale than previously reported.[26] First, oleic acid (57.98 mL, 0.231 mol) was mixed with a small excess of NaOH (12.74 g, 0.319 mol) dissolved in 800 mL MilliQ water at 45 °C for 3 h in a 1 L flask. Afterwards, $[P_{8888}][Br]$ (100 g, 0.177 mol) was added to the reaction mixture and the mixture was stirred for an additional 6 h at 75 °C. The organic phase was then washed multiple times with water (6 x 500 mL) and remaining water was removed by a rotary evaporator (BUCHI Rotavapor® R-3) and a vacuum oven at 50 °C to obtain a slightly yellow viscous liquid as product (135.1 g). The yield was 99%. The bromide content was 5 $\mu g \cdot mL^{-1}$. The IL was determined by ^{1}H NMR (Bruker 400 MHz, $CDCl_3$, δ/ppm) and the following data was obtained: δ = 0.88 (m, 15H), 1.26 (m, 54H), 1.48 (m, 14H), 1.60 (m, 2H), 1.99 (m, 4H), 2.17 (t, 2H), 2.37 (m, 8H), 5.32 (m, 2H). MS (ESI) was run and the following data was obtained: $[P_{8888}(C_{32}H_{68}P)]^+$ m/z = 483.6 (calculated value m/z = 483.9) and [oleate $(C_{18}H_{33}O_2)]^-$ m/z = 281.3 (calculated m/z = 281.5).

Experimental setup

Figure 6.1 presents a schematic drawing of the continuous setup, in which one can observe two mixer-settler extractors placed in series. The solutions are pumped into the extractors using 8 mm pipes. *Masterflex L/S* pumps were set for the first experiment at 15 $mL \cdot min^{-1}$ to get an accurately regulated flow of IL, aqueous metal solution and stripping solution in the set up. This flow rate made sure that the IL had a contact time of more than 4 min with the aqueous metal salt solution or aqueous stripping solution in the mixers, which is minimum time necessary to reach the equilibrium state for the extraction.[26] For the second experiment the flow rate of the pumps was set at 20 $mL \cdot min^{-1}$. Two pumps were placed at the outlet of both settlers, which stabilized the height at which phase disengagement of the IL and water phase occurred. Mixing was done with magnetic mixing rods and the mixing plates (Heidolph MR Hei-Mix S) were set at 1200 rpm to allow rigorous mixing.

First a continuous metal extraction experiment was performed with a solution consisting of 1.0 $g \cdot L^{-1}$ Co and 1.0 $g \cdot L^{-1}$ Na (Co/Na) from the corresponding chloride salts for 165 min. Afterwards, the experiment was repeated with a solution consisting out of 1.0 $g \cdot L^{-1}$ cobalt, 1.0 $g \cdot L^{-1}$ potassium and 1.0 $g \cdot L^{-1}$ calcium (Co/K/Ca) from their chloride salts for 300 min. A 0.1 M aqueous sodium oxalate water solution was each time applied as stripping solution. IL was first water saturated before being applied in the continuous process. The whole setup was first half filled with MilliQ water (±200 mL) and afterwards ±200 mL of water saturated IL was pumped into the setup. At the start of the experiments all pumps were turned on and all operated at the same speed.

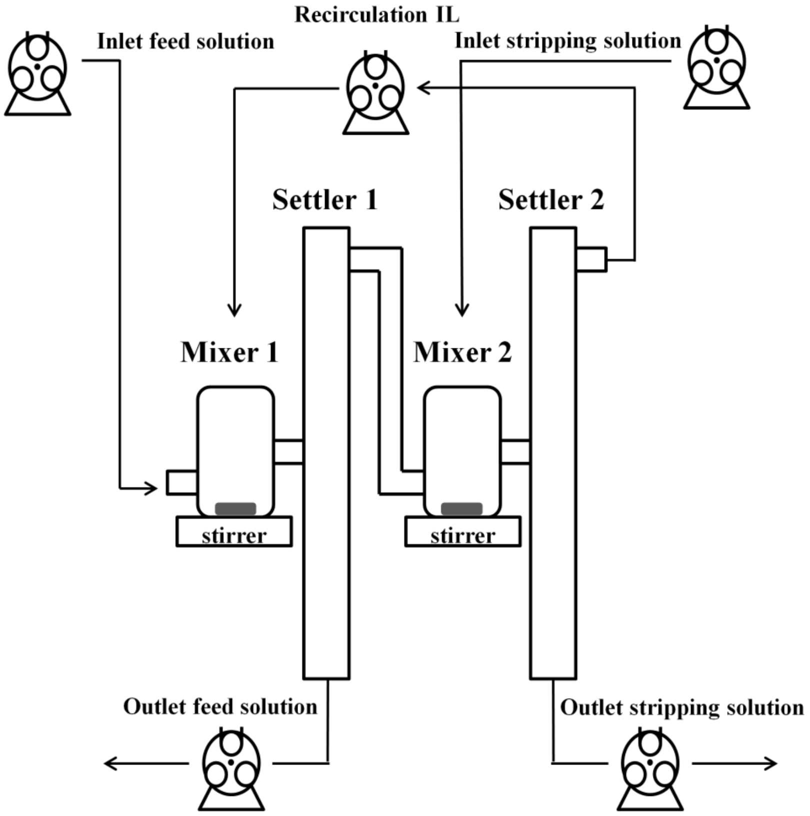


***Figure 6.1**. Schematic drawing of setup applied for the continuous process of selective metal extraction and IL regeneration.*

Analysis of the aqueous metal solution and stripping solution

The aqueous metal solution and stripping solution were analysed before and after going through the continuous process for selective metal extraction. Every half hour 30 mL of sample was taken at the outlets of the aqueous metal solution and the stripping solution after it passed through the continuous process. The cation and anion concentration, pH, total organic carbon (TOC), inorganic carbon (IC) and total carbon (TC) were measured from these samples. For the cation analysis a Perkin Elmer precisely inductively coupled plasma spectroscopy (ICP) was used, which used an optical atom emission spectrometer (OES) Optima 5300DV. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-OES has a detection limit of 25-250 $\mu g \cdot L^{-1}$ and an uncertainty of 1.4-2%. Anion concentration analysis was done on a Metrohom 761 Compact ion chromatograph (IC) system equipped with a 762 IC interface which had a detection limit of 0.1 $mg \cdot L^{-1}$.

Extraction efficiencies (*E*) were calculated by:

$$E(\%) = \frac{\left((\mathrm{c_{0aq}} - \mathrm{c_{1aq}}) * \mathrm{F_{outled\ feed}}\right)}{\mathrm{c_{0aq}} * \mathrm{F_{inlet\ feed}}} \text{ x } 100 \qquad (1)$$

where $c_{0\mathrm{aq}}$ and $c_{1\mathrm{aq}}$ are the total metal concentrations in the aqueous phase before and after metal extraction in the first mixer settler occurred. $F_{\mathrm{inlet\ feed}}$ equals the volume flow rate of the aqueous feed solution at the inlet of the first mixer and $F_{\mathrm{outlet\ feed}}$ equals the volume flow rate of the aqueous feed solution at the outlet of first settler.

The stripping (S) efficiency was determined by equation 2:

$$S(\%) = \frac{(c_{2aq} * F_{outlet\,stripping})}{(c_{0aq} * F_{inlet\,stripping})} \text{ x } 100 \qquad (2)$$

in which $c_{2\mathrm{aq}}$ is the metal concentration in the aqueous phase after the stripping occurred in the second mixer settler and $c_{0\mathrm{aq}}$ stands again for the concentration of ions in the start solution. $F_{\mathrm{inlet\ stripping}}$ equals the volume flow rate of the cobalt loaded IL solution at the inlet of the second mixer and $F_{\mathrm{outlet\ stripping\ solution}}$ equals the volume flow rate at of the aqueous stripping solution at the outlet of the second settler.

The pH of the water phase was measured after the metal extraction experiment with a Metrohm 827 lab pH meter. The solubility of the IL in the water phases was measured by TOC, IC and TC analysis using a Shimadzu TOC-LCPH with a detection limit of 1.00 $\mathrm{mg{\cdot}L^{-1}}$.

Critical micelle concentration determination of the IL

In order to get some information on the aggregation behaviour of the IL, the critical micelle concentration (CMC) of the IL in water was determined. The surface tension measurements were performed with a pendant drop method at room temperature using a CAM 200 Optical Contact Angle Meter (Biolin Scientific, KSV Instruments, Finland) equipped with a CCD Video Camera Module. Evaluation of data was performed using the Attension Theta Software (ver. 4.1.0, Biolin Scientific, Finland) with the frame interval of 1 s and 20 frames collection. Fitting of collected images was done using the Young-Laplace equation.

Liposome preparation

Liposomes were prepared by mixing stock solutions of eggPC (20 mM) and POPG (15 mM) to yield a total concentration of 3.0 mM. The appropriate mixing ratio of lipid stocks in chloroform was 75/25 (mol%) of eggPC/POPG. The resulting mixture was evaporated to dryness under a stream of pressurized air, and solvent residues were removed by evacuation under reduced pressure (8–100 mbar) for at least 16 h. The lipid residues were hydrated in the sodium phosphate buffer at 60 °C for 60 min with shaking to yield multi-lamellar vesicles. The resulting dispersion was processed to give large uni-lamellar vesicles by extruding the mixture 19 times through Millipore (Bedford, MA, USA) 100-nm pore size polycarbonate filters using a Liposo-Fast extruder. The sizes were routinely confirmed by Malvern Zeta Sizer (data not shown).

Zeta potential determinations

Laser Doppler micro-electrophoresis, using a Malvern Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) instrument, was used to measure the zeta potentials (surface charge) of the liposomes. Measurements were conducted in disposable folded capillary cells for zeta potential (surface charge) measurements. The liposome dispersion was diluted to a concentration equal to 0.1 mM. The IL was added to the liposome at various concentrations, in the range of 0-900 μM. The solvent for both liposomes and IL was a phosphate buffer at pH 7.4 (ionic strength of 10 mM). The samples were degassed using a vacuum degasser.

Long term stability experiment

Different [P_{8888}][oleate] IL samples were left open to air at room temperature for a period of 3 months and periodically analyzed by electrospray ionisation mass spectrometry (ESI-MS) to determine its stability. The samples were pure IL, IL with an excess of water and IL after the extraction of cobalt that was left in contact with the water phase originally containing 1.0 $g{\cdot}L^{-1}$ of Co from its chloride salt. At defined intervals (start of the experiment, after 2 weeks, after 2 months, after 3 months) samples were taken. An Agilent Technologies 1200 series ESI-MS was applied with acetonitrile:water 90:10 v/v ratio as eluens working with an Agilent MassHunter workstation data acquisition. Also, ^{1}H NMR analysis was performed on a Bruker 400 MHz NMR on the IL before and after being applied in the continuous process. Additionally, the kinematic viscosity of the IL after the second continuous metal extraction experiment was determined at 25 °C using a capillary viscometer 50120 of Schott Instruments.

6.3. Results and discussion

Continuous extraction study

[P_{8888}][oleate] was selected as the extracting phase, both acting as a solvent and as the extractant for selective removal of transition metal ions from an aqueous metal salt solution. Previous research demonstrated that this IL was very hydrophobic, so that losses into the water phase are minimized.[26] Moreover, it was shown that [P_{8888}][oleate] can selectively extract metals depending on pH and chloride concentration and it has a low viscosity, even at room temperature.[26,29] Therefore, this metal extraction process can be operated at room temperature with high enough extraction rates, which is a significant improvement and saving in energy cost compared to other IL metal extraction systems in which the water phase needs to be heated to elevated temperatures ($\geq$40 °C).[28] Based on previous results, sodium oxalate was selected as the optimal stripping solution.[27] Although this stripping solution does not completely regenerate the IL phase, it allows reuse of the IL. In addition, sodium oxalate is safe to use, making this continuous extraction/regeneration process easier to operate compared to other systems, which generally apply strong acids or bases for the regeneration.[30–33] The process applied for continuous metal extraction is shown in Figure 6.2. Cobalt was the preferred transition metal of choice for selective extraction, because of the nice visible colour it has in the aqueous phase (red/pink) and in the IL phase (dark blue).

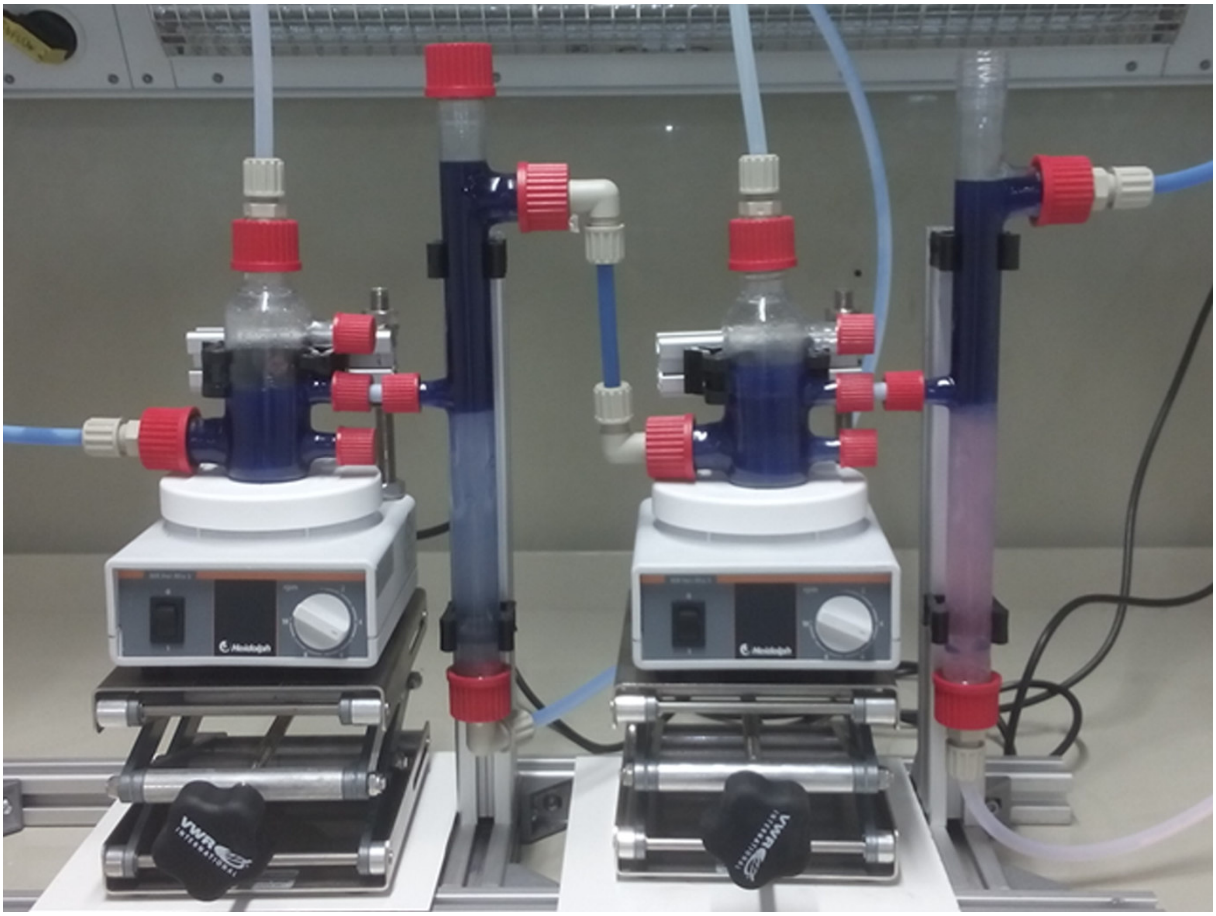


Figure 6.2. *Setup in which the continuous process for selective metal extraction was operated. It existed out of two mixer-settlers for selective removal of transition metals out of an aqueous salt stream by applying the ionic liquid tetraoctylphosphonium oleate.*

In the first mixer, recirculated IL is mixed with the aqueous metal solution to perform selective metal extraction. At the start of each experiment a colour change of the IL from slight yellow towards dark blue was immediately observed due to the extraction of cobalt. Afterwards, the mixed aqueous IL solution underwent phase separation in the first settler. Clear transparent water from which the valuable cobalt salt is extracted is then obtained at the bottom of the first settler. IL loaded with cobalt is collected at the top and flows into the second mixer, in which it is mixed with the stripping solution. Phase disengagement then occurs in the second settler to obtain a pink water phase due to the back extraction of cobalt by oxalate. The IL phase is then recirculated to the first mixer, so that it can be reused. The colour of the IL after stripping still remained blue, because the cobalt loaded IL was only partially removed from the IL.

Table 6.1. *Chloride, sodium and cobalt concentration and pH of the feed solution and stripping solution.*

	Cl (mg L^{-1})	Na (mg L^{-1})	Co (mg L^{-1})	pH
Feed solution	2775	918	921	6.2
Stripping solution	<20.0	>2000	<5	9.6

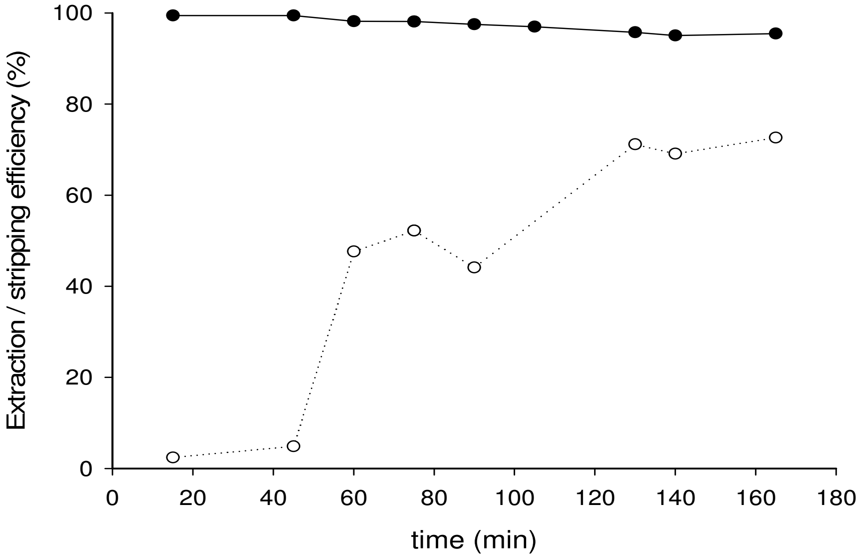


Figure 6.3. *Extraction efficiency (●) and stripping efficiency (○) of the continuous metal extraction process operated with a stream of 1.0 g·L^{-1} Co/Na chloride at a flow rate of 15 mL·min^{-1} for the whole process.*

The first continuous metal extraction experiment was performed with a Co/Na feed solution presented in Table 6.1, which had a molar ratio of 0.39 for Co/Na. The flow rate of all solutions was 15 mL·min^{-1}. Results of the extraction efficiency and stripping efficiency are presented in Figure 6.3. Figure 6.3 clearly shows that the extraction efficiency of cobalt remained high (>95%) during the 165 min of experimentation; there was only a small decrease in extraction efficiency over time. No extraction of sodium was observed. Results of the stripping solution indicate that the stripping solution was getting more concentrated in cobalt over time. A small decrease in pH was observed at the beginning of the experiment (Figure 6.4), but after about 60 min of operation the pH became stable. After 45 min minutes operation the average pH value was 8.3 for the feed solution and 9.1 for the stripping solution.

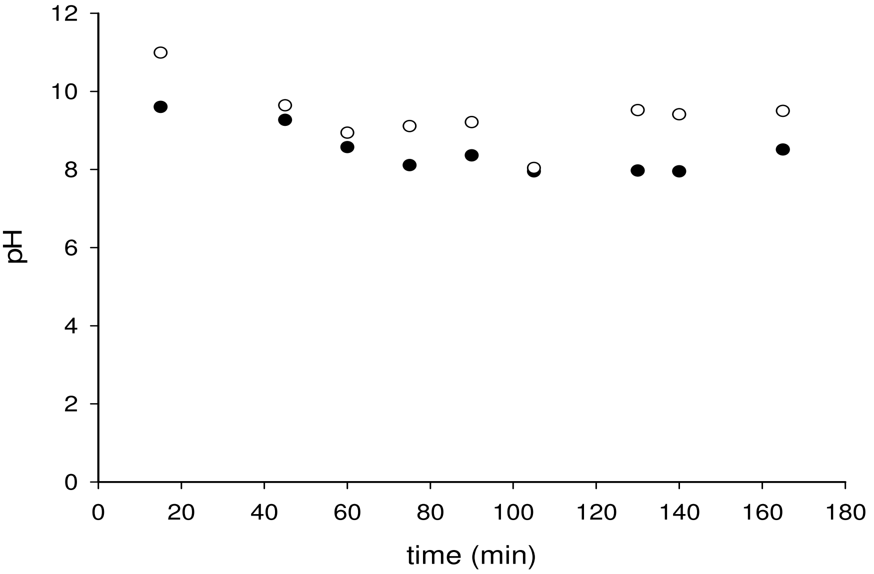


Figure 6.4. *pH values for the feed solution (●) and stripping (○) solution for continuous metal extraction of the Co/Na stream over time.*

Encouraged by the promising results obtained in the first experiment (see Figure 6.3), a second experiment was performed with a Ca/Co/K feed solution presented in Table 6.2 with a flow rate of 20 $mL\cdot min^{-1}$ for 5h. Molar ratio for the feed Ca/Co/K stream is 1.50:1.0:1.58. This feed solution was chosen to investigate the selectivity of the IL [P_{8888}][oleate] for transition metals over alkali and earth alkali metals over time. From the results in Figure 6.5, it is observed that the IL shows excellent extraction efficiencies (t = 15 min, 96 %) at the beginning of the experiment, but decreases within 2h to an extraction efficiency that remains constant around 54%. At the beginning, also some extraction of calcium is observed (t = 15 min, 21%), but this rapidly declines. On average, low and negligible extraction efficiencies are observed for calcium (6%) and potassium (4%), proving the preference of the IL [P_{8888}][oleate] for the transition metal cobalt. Sodium concentration in the feed solution after extraction was around 25 $mg\cdot L^{-1}$, indicating that the extraction mechanism is not based on ion-exchange of sodium ions for cobalt ions. It is assumed that the lower extraction efficiency over time for cobalt compared to the first experiment is due to the higher flow rate of all streams (20 $mL\cdot min^{-1}$ compared to 15 $mL\cdot min^{-1}$), indicating that the contact time between the IL and the feed and stripping solution is a key factor. Nevertheless, it is very positive to notice that the extraction efficiency for cobalt stays stable over time, indicating that the extraction and stripping in the process reaches a stable equilibrium and that there is no degradation of the IL occurring that prevents further metal extraction.

Results of the ion concentration from the consumed stripping solution are presented in Figure 6.6. The results in Figure 6.6 show that on average a 543 ±57 mg·L^{-1} cobalt stream with an impurity of 56 ±19 mg·L^{-1} calcium was obtained starting from a 987 ±18 mg·L^{-1} calcium, 1013.5 ±23 mg L^{-1} potassium and 969.5 ±16 mg·L^{-1} cobalt feed stream. Results of potassium are not presented in Figure 6.6, because the concentration of potassium in the stripping solution was at or below the detection limit (10 mg·L^{-1}). Result of the obtained cobalt concentration in the stripping solution is in good agreement with the calculated amount of cobalt extracted (512 ±36 mg·L^{-1}; average concentration of cobalt extracted is determined from the average cobalt concentrations obtained between two and five hours of experiments, when the system reached its equilibrium state.) Results of the pH presented in Figure 6.7 indicate that the pH of both aqueous solutions remained constant after being applied in the continuous metal extraction process. On average the feed solution after IL extraction had a stable pH of 7.8 and for the stripping solution a stable pH of 8.8 was observed. Also, the total organic carbon (TOC) content was measured in both solutions after contact with the IL (see supplementary information). The TOC content in the feed solution turned out to be ≤14 mg·L^{-1}, showing that the leakage of IL going to the water phase is very small (≤18 mg IL·L^{-1}) and even some of the measured TOC in this solution can be originating from oxalate that was still in the IL. The stripping solution already contained 2440 mg·L^{-1} organic carbon at the start of the experiment due to the dissolved sodium oxalate. During the experiment the organic carbon content in the stripping solution fluctuated, but was on average 2414 mg·L^{-1}, again indicating that only very small losses occurred.

Table 6.2. *Chloride, calcium, potassium, sodium and cobalt concentration and pH of the feed solution and stripping solution at the start of the experiment.*

	Cl (mg L^{-1})	Ca (mg L^{-1})	K (mg L^{-1})	Na (mg L^{-1})	Co (mg L^{-1})	pH
Feed solution	3675	987	1013.5	<50	969.5	5.97
Stripping solution	<20.0	<10	<10	>1000	<2.5	9.5

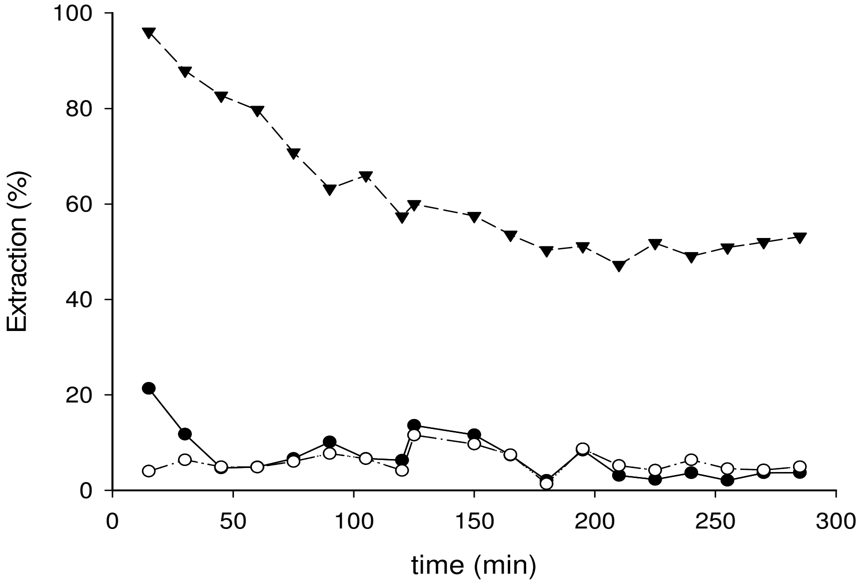


Figure 6.5. *Extraction efficiencies as a function of time for the Ca(●)/Co(▼)/K(○) feed solution after metal extraction in the continuous process at a flow rate of 20 mL·min^{-1} for the whole process.*

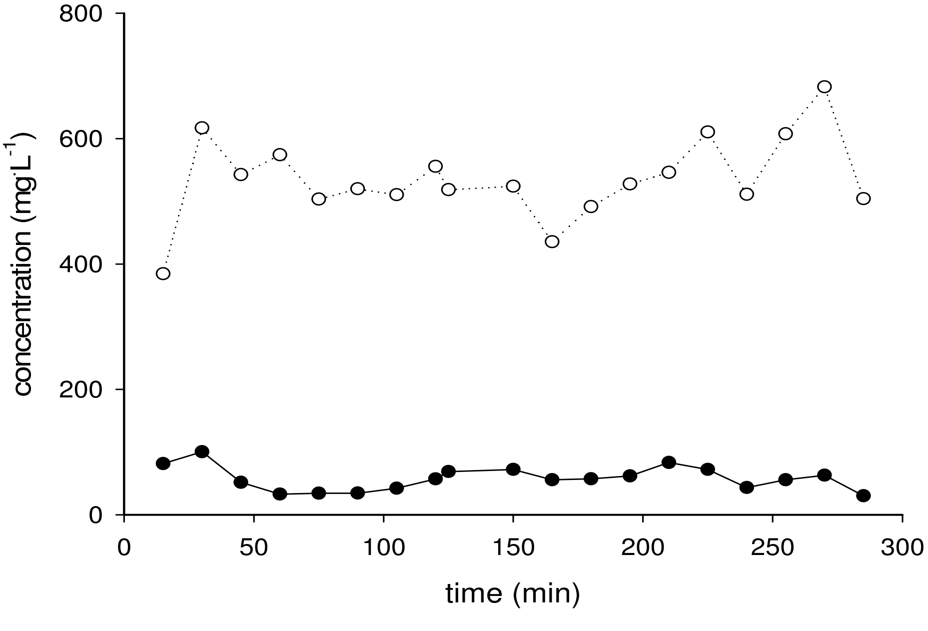


Figure 6.6. *Change of metal ion concentration as a function of time in the stripping solution for Co(○) and Ca(●) after being applied in the continuous process.*

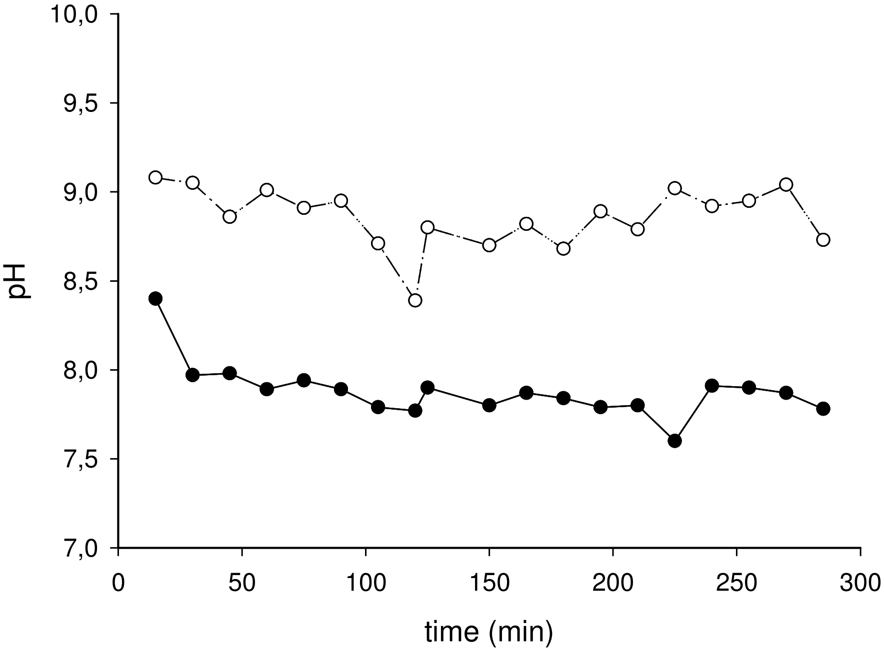


Figure 6.7. *pH values for the feed solution(●) and stripping solution(○) after being applied in the continuous metal extraction process as a function of time.*

Interactions of the ionic liquid with liposomes

Interactions between ILs and cells as well as bio-mimetic liposomes have been studied to some extent.[34–36] In those studies the focus has been on determining the toxicity of the ILs towards biological systems. It was shown that branched ions of the ILs can exert their toxic effect due to their ability to penetrate into the lipid bilayer, which furthermore causes membrane-bound protein disruption.[37,38] Mikkola *et al.* recently demonstrated that human corneal epithelial cells and E. coli bacterial cells were strongly affected by the type and concentration of the ILs studied.[36] Shorter-chain amidinium and imidazolium ILs showed no clear effect on the cells, whereas most of the longer-chain phosphonium ILs were highly toxic. Tested longer-chain phosphonium ILs were tributyl(tetradecyl)phosphonium chloride ([P_{14444}]Cl), tributyl(tetradecyl)phosphonium acetate ([P_{14444}][OAc]) and trihexyl(tetradecyl)-phosphonium acetate ([P_{14666}][OAc]) and these ILs had a CMCs of 0.3 mM, 0.3 mM and 0.1–0.2 mM in a 10 mM sodium phosphate buffer, respectively . The concentration of IL at which the surface charge of the liposomes changed was 0.230 and 0.218 mM for [P_{14444}]Cl and [P_{14444}][OAc], respectively.[36] Regarding the toxicity of the IL [P_{8888}][oleate] towards the cells, the CMC of the long-chain phosphonium ILs was in the concentration range of the toxicity, suggesting some kind of a relationship between the CMC of the IL and its toxicity. In this work the CMC of the IL was determined by the pendant drop method. The obtained value for the CMC was 6.72 μM. This very low value demonstrates the highly hydrophobic nature of the IL. Changes in the surface charge (zeta potential) of negatively charged liposomes upon addition of various concentrations of the IL (0-900 μM) were followed and the results are shown in Figure 6.8. There is a big change in the surface charge of the liposome, indicating strong electrostatic and hydrophobic interactions. The saturation level is around 250 μM of added IL. These data give us an idea about the effect of the IL on biological systems and clearly shows that the IL is highly hydrophobic and eager to interact with negatively charged liposomes, used as good bio-mimicking models. This indicates that the IL $[P_{8888}]$[oleate] also has a high toxicity towards cells because of its high lipophilicity, although it consists of an biodegradable anion and has a very low solubility in water.

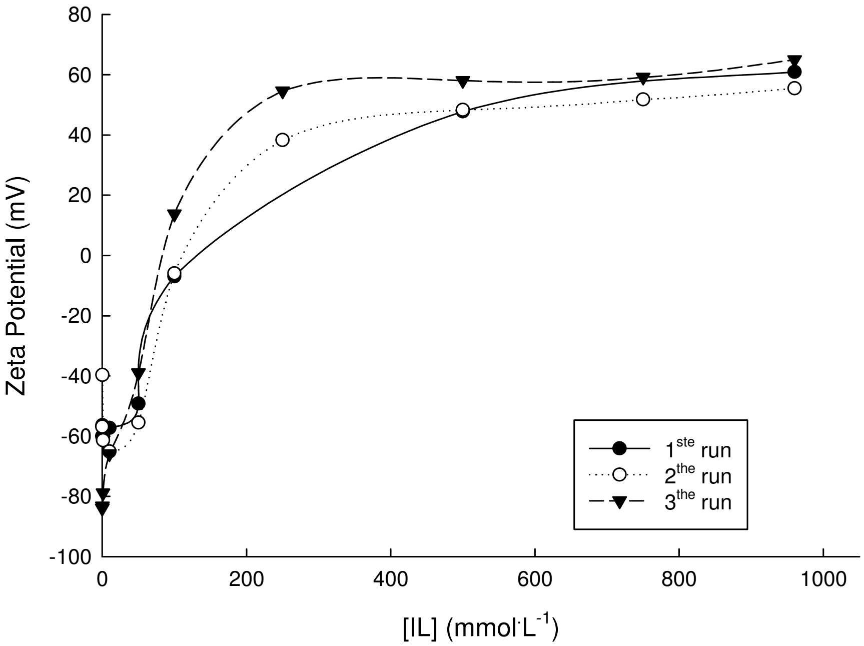


Figure 6.8. *Zeta potentials of 75/25 mol% eggPC/POPG liposomes upon addition of* $[P_{8888}]$*[oleate].*

Stability of the ionic liquid

An often heard concern about applying fatty acid based ILs is their chemical stability. Therefore, an additional experiment was performed in which different $[P_{8888}]$[oleate] IL samples were left open to air for a period of 3 months and periodically analyzed via ESI-MS (see supplementary information). The samples were pure IL, IL with an excess of water and

IL after the extraction of cobalt that was left in contact with a water phase originally containing 1.0 $g \cdot L^{-1}$ of Co from its chloride salt. For all these samples no changes in the MS spectra were observed for the whole duration of the experiment. Also, a ^{1}H NMR spectrum of the IL that was applied for extraction of the Ca/Co/K feed solution was taken before and after usage (see supplementary information), indicating that except for the broadening of the peaks due to interaction of water and cobalt with the IL, no changes or additional peaks were observed in the NMR spectra. Moreover, the kinematic viscosity of the IL was determined after being applied in the continuous process and turned out to be 162 $mm^{2} \cdot s^{-1}$. Comparing this value with the viscosity obtained for the full water saturated [P_{8888}][oleate] (156 $mm^{2} \cdot s^{-1}$) shows no significant difference. The sample to determine the viscosity was taken from the second settler, indicating that the small increase in viscosity is most likely due to cobalt remaining in the IL. All these results indicate that there is no significant degradation occurring at the conditions applied (room temperature, pH 5.9-9.6) for continuous metal extraction.

Economic analysis of the continuous extraction process

The fatty acid based IL used in this research was designed to treat water, while minimizing the risk of polluting the water with toxic organic compounds. This has as consequence, due to the oxidative reactivity of the anion of [P_{8888}][oleate], that this IL is not suitable for long-term operation at low (<4) or high (>8) pH and at high temperatures (>50 °C). Treatment of metal polluted water by this IL is only applicable for water with a pH ranging from 4-8. This makes the process less applicable for highly acidic water, which can contain high concentrations of dissolved transition metals. Instead, the developed process is more relevant for treatment of wastewater containing low transition metal ion concentrations. Biggest advantage of this process compared to other continuous metal extraction process with ILs reported in literature is that the complete process can be operated at room temperature, resulting in an enormous saving in energy cost.[28]

Although the IL [P_{8888}][oleate] can extract multiple transition metals and rare earth metals,[26] a cobalt waste stream was chosen as subject for an economical analysis with this system due to the similarity with the lab experiment. Cobalt can be found in the waste streams of nuclear power plants and in many industries such as mining, metallurgical, electroplating, paints, pigments and electronic industry. In literature, an example of a cobalt (Co) polluted waste stream from the paint industry can be found, which also contained the metals lead (Pb) and cadmium (Cd).[39] In 2008, this industry with a 70 ton/month paint production had approximately 200 m^3/month wastewater production. Table 6.3 presents the data of their waste water, which was used for the economic analysis in this study.

Table 6.3. Waste water characteristics of Binalood Paint Industries[39]

Parameters	Mean	SD	Unit
pH	5.5	1.5	pH unit
BOD	252.5	20.9	$mg \cdot L^{-1}$
COD	610	32.47	$mg \cdot L^{-1}$
TSS	102.5	13.9	$mg \cdot L^{-1}$
TDS	3325	491.05	$mg \cdot L^{-1}$
EC	1750	217.3	$\mu S \cdot cm^{-1}$
Pb	5.4	1.3	$mg \cdot L^{-1}$
Co	1.15	0.26	$mg \cdot L^{-1}$
Cd	1.6	0.29	$mg \cdot L^{-1}$

BOD = biological oxygen demand, COD = chemical oxygen demand, TSS = total suspended solids, TDS = total dissolved solids, EC = electrical conductivity

Heavy metals such as cobalt are nowadays often removed by applying ion-exchange resins (IER). Although IER sometimes show a very high selectivity towards specific metals, they cannot be operated in a continuous mode. Furthermore, recovery of the metals and reuse of the resins is not always easily achieved. Still, a comparison of the continuous IL process in this work with a commercial IER that is selective for heavy metals (Purolite® S924) is made for the waste stream presented in Table 6.3. It is anticipated that both processes need the same pre-treatment steps to remove the organics from the total dissolved solids (TDS) in the water. The organics, that are partially soluble in water and contain charged functional groups, will most likely be extracted into the ILs phase (continuous IL process) or induce fouling (IER).

The economical analysis was performed for both systems (see supplementary information). It was shown that the capital expenditure (CAPEX) of the continuous IL based process for the treatment of this specific waste water is expected to be 33% more expensive than two IER columns in parallel (€ 68370 for the IL system compared to € 45100 for IER). The reason is that the IER for the removal of heavy metals cost € 25 /kg, which is somewhat lower than the assumed IL cost price at large scale production (€ 33.7 /L)(see supplementary information).[40] The operational cost for the IL process are also more expensive and this is mainly due to the consumption of high volumes of the stripping solution (the operational expenditures (OPEX) for the extraction and regeneration are € 8.23 /L for the IL system, while this is only € 0.73 /L for IER). Leakage of IL to the water phase should also be minimized over time by for example the implementation of filters/membranes at the outlet of the settlers, else the operation cost will further increase. Therefore, at the moment the IL process is not yet economically viable, especially if the only purpose of the process is to purify water by salt extraction. Nevertheless, continuous IL metal extraction systems can become a very good option if one also looks at the costs of brine disposal and the recovery and valorisation of valuable metals from waste water.

6.4. Conclusions

In this work we demonstrate that it is technically possible to operate a continuous process for selective metal extraction based on the IL [P_{8888}][oleate]. Good and stable extraction efficiencies were obtained in which excellent selectivity for cobalt was observed. For example, when working with a feed stream containing 1.0 $g \cdot L^{-1}$ of the metals Ca/Co/K, a concentrated cobalt stream was obtained containing 543 $mg \cdot L^{-1}$ of Co, 56 $mg \cdot L^{-1}$ of Ca and no detectable K. It was also noticed that the contact time of the IL for extraction and stripping determined the achieved efficiencies. Furthermore, it was demonstrated that the fatty acid based IL was stable for the duration of the experiment. Although this IL is very hydrophobic and consist out of a natural fatty acid as anion, it strongly interacts with bio-mimicking liposomes due to its liphophilic character. Economic analysis shows that the IL based process that was developed was both more expensive in CAPEX and OPEX compared to ion-exchange resins, especially in case demineralised water is the only product. However, if the recovery of valuable metals is also taken into account and/or in case brine disposal is an issue, then continuous IL metal extraction systems are a promising alternative.

6.5. References

1 P. H. Gleick, in *Water in crisis: a guide to the world's fresh water resources.*, Oxford University Press, Inc., 1993, pp. 13–24.
2 J. A. A. Jones, *Water sustainability: a global perspective*, Routledge, 2014.
3 R. Collins, P. Kristensen and N. Thyssen, *Water resources across Europe — confronting water scarcity and drought*, European Environment Agency, 2009.
4 S. Chakrabarty and H. P. Sarma, *Environ. Monit. Assess.*, 2011, **179**, 479–86.
5 W. H. Organization, *WHO | Guidelines for drinking-water quality - Volume 1: Recommendations*, World Health Organization, 2008.
6 European Commision, *Report on critical raw materials for the EU*, 2010.
7 J. Rydberg, M. Cox, C. Musikas and G. R. Choppin, *Solvent Extraction Principles and Practice, Revised and Expanded*, CRC Press, 2004.
8 C. F. Coleman and J. W. Roddy, *Solvent Extr. Rev.*, 1971, **1**, 63–91.
9 E. P. Horwitz, M. L. Dietz and D. E. Fisher, *Solvent Extr. Ion Exch.*, 1990, **8**, 199–208.
10 F. G. Seeley and D. J. Crouse, *J. Chem. Eng. Data*, 1971, **16**, 393–397.
11 J. S. Preston, *Hydrometallurgy*, 1985, **14**, 171–188.
12 A. G. Chmielewski, T. S. Urbański and W. Migdał, *Hydrometallurgy*, 1997, **45**, 333–344.
13 J. Cui and L. Zhang, *J. Hazard. Mater.*, 2008, **158**, 228–56.
14 F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407–418.
15 M. A. Barakat, *Arab. J. Chem.*, 2011, **4**, 361–377.
16 T. A. Kurniawan, G. Y. S. Chan, W. Lo and S. Babel, *Sci. Total Environ.*, 2006, **366**, 409–26.
17 S.-Y. Kang, J.-U. Lee, S.-H. Moon and K.-W. Kim, *Chemosphere*, 2004, **56**, 141–7.
18 H. M. A. Rossiter, P. A. Owusu, E. Awuah, A. M. Macdonald and A. I. Schäfer, *Sci. Total Environ.*, 2010, **408**, 2378–86.
19 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2012.
20 R. D. Rogers and G. A. Voth, *Acc. Chem. Res.*, 2007, **40**, 1077–1078.
21 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73–80.
22 L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water Res.*, 2011, **45**, 4601–4614.
23 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.
24 A. Rout, J. Kotlarska, W. Dehaen and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16533–16541.
25 F. Pena-Pereira and J. Namieśnik, *ChemSusChem*, 2014, **7**, 1784–800.
26 D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans and M. C. Kroon, *Ind. Eng. Chem. Res.*, 2015, **54**, 5149–5158.
27 D. Parmentier, Y. A. Valia, S. J. Metz, O. S. Burheim and M. C. Kroon, *Submitt. to Hydrometall.*
28 S. Wellens, R. Goovaerts, C. Moeller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.
29 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.
30 P. Nockemann, B. Thijs, S. Pittois, J. Thoen, C. Glorieux, K. Van Hecke, L. Van Meervelt, B. Kirchner and K. Binnemans, *J. Phys. Chem. B*, 2006, **110**, 20978–20992.
31 B. Onghena, J. Jacobs, L. Van Meervelt and K. Binnemans, *Dalt. Trans.*, 2014, **43**, 11566.
32 a. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, 2011, **80**, 385–389.
33 M. Regel-Rosocka, *Sep. Purif. Technol.*, 2009, **66**, 19–24.
34 T. P. T. Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–72.
35 A. Sosnowska, M. Barycki, M. Zaborowska, A. Rybinska and T. Puzyn, *Green Chem.*, 2014, **16**, 4749–4757.
36 S.-K. Mikkola, A. Robciuc, J. Lokajová, A. J. Holding, M. Lämmerhofer, I. Kilpeläinen, J. M. Holopainen, A. W. T. King and S. K. Wiedmer, *Environ. Sci. Technol.*, 2015, **49**, 1870–1878.
37 D. W. Roberts, *Sci. Total Environ.*, 1991, **109-110**, 557–568.
38 D. Roberts and J. Costello, *QSAR Comb. Sci.*, 2003, **22**, 220–225.
39 M. Malakootian and H. Hossaini, *Int. J. Sci. Technol.*, 2008, **5**, 217–222.
40 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

Supplementary info

SI.6.1. TOC analysis

Total organic carbon (TOC) analysis was performed on the samples taken from the feed and stripping solution of the experiment that was treating a Ca/Co/K chloride slat solution at velocity of 20 mL·min^{-1}. Indicating that the TOC content in the feed solution at the start was 3.08 mg·L^{-1} and the average TOC concentration in the feed solution after being treated in the continuous setup turned out to be ≤14 mg·L^{-1}. The stripping solutions contained already 2440 mg·L^{-1} organic carbon at the start of the experiment due to the dissolved sodium oxalate. During the experiment the organic carbon content in the stripping solution fluctuated, but was on average 2414 ±91 mg·L^{-1}.

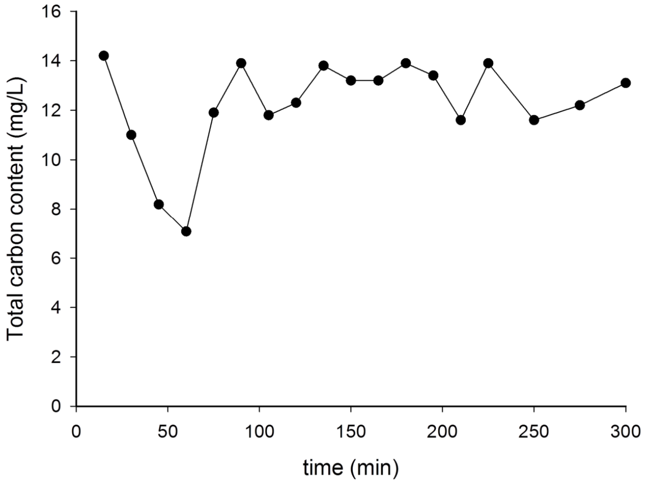


Figure SI.6.1. Total carbon content in the Ca/Co/K feed stream as a function of the operation time.

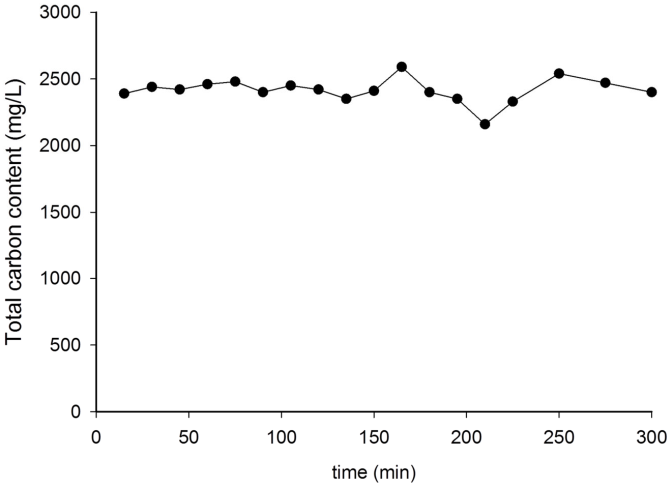


Figure SI.6.2. Total carbon content in the stripping solution as a function of the operation time.

SI.6.2. Stability experiment

3 samples of the $[P_{8888}]$[oleate] IL were left open to air for a period of 3 months to determine its long term stability. The samples were pure IL, IL with an excess of water and IL after the extraction of cobalt that was left in contact with the water phase originally containing 1000 $mg{\cdot}L^{-1}$ of Co from its chloride salt. Periodically (start, 2 weeks, 2 months and 3 months) the samples were analyzed via ESI-MS. No change in MS spectra was observed during for the duration of the experiment. Also an MS spectrum was taken from the IL after being applied for 300 min in the continuous metal extraction setup. MS spectrum calculated for $[P_{8888}(C_{32}H_{68}P)]^+$ gives $m/z = 483.9$ and calculated for [Oleate $(C_{18}H_{33}O_2)]^-$ gives $m/z = 281.5$.

-Start of the experiment

MS (ESI): Positive spectrum: for the pure IL $m/z = 483.7$, IL with water $m/z = 483.6$ and IL with cobalt $m/z = 483.6$ and for the negative mode: for the pure IL $m/z = 281.3$, IL with water $m/z = 281.3$ and IL with cobalt $m/z = 281.3$.

-After 2 weeks

MS (ESI): Positive mode: for the pure IL $m/z = 483.6$, IL with water $m/z = 483.5$ with an additional peak at 1012.0 ($2 \times [P_{8888}]^+ + [\text{formate}]^-$) and IL with cobalt $m/z = 483.5$ and for the negative mode: for the pure IL $m/z = 281.2$, IL with water $m/z = 281.2$ and IL with cobalt $m/z = 281.2$. Additional peaks were observed in all three spectra 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 eluens of the LC-MS.

-After 2 months

MS (ESI): Positive mode: for the pure IL $m/z = 483.6$, IL with water $m/z = 483.5$ with an additional peak at 1012.0 ($2 \times [P_{8888}]^+ + [\text{formate}]^-$) and IL with cobalt $m/z = 483.5$ and for the negative mode: for the pure IL $m/z = 281.2$, IL with water $m/z = 281.2$ and IL with cobalt $m/z = 281.2$. Additional peaks were observed in all three spectra 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 eluens of the LC-MS.

-After 3 months

MS (ESI): Positive mode: for the pure IL *m/z* = 483.5 , IL with water *m/z* = 483.5 with an additional peak at 1012.0 (2 × $[P_{8888}]^+$ + $[\text{formate}]^-$) and IL with cobalt *m/z* = 483.5 and for the negative mode: for the pure IL *m/z* = 281.2, IL with water *m/z* = 281.2 and IL with cobalt *m/z* = 281.2. Additional peaks were observed in all three spectra in the negative mode: 573.5 ($[P_{8888}]^+$ + 2 × $[\text{formate}]^-$), 809.7 ($[P_{8888}]^+$ + $[\text{oleate}]^-$ + $[\text{formate}]^-$), 1046.0 ($[P_{8888}]^+$ + 2 × $[\text{oleate}]^-$), formic acid is for 1% present in the eluens of the LC-MS.

-ESI-MS spectra of the IL after being applied in the continuous metal extraction setup
MS (ESI): Positive mode for the IL gives a peak at *m/z* = 483.5 with an additional small peak at 1001.9 (2 × $[P_{8888}]^+$ + $[\text{Cl}]^-$) and for the negative mode a peak is observed for the IL at *m/z* = 281.2 with additional peaks at 573.4 ($[P_{8888}]^+$ + 2 × $[\text{formate}]^-$), 809.7 ($[P_{8888}]^+$ + $[\text{oleate}]^-$ + $[\text{formate}]^-$), 1045.9 ($[P_{8888}]^+$ + 2 × $[\text{oleate}]^-$), formic acid is for 1% present in the eluens of the LC-MS.

SI.6.3. ^{1}H NMR spectra of the IL before and after usage in the continuous setup

^{1}H NMR spectra were taken of different NMR samples to investigate the stability of the IL when being applied in the continuous metal extraction setup. Except for the broadening of the peaks due to the interaction of water and cobalt in the IL from the continuous metal setup, no changes or additional peaks were observed in the NMR spectra.

NMR spectra theoretically

^{1}H NMR: δ = 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)

NMR spectra freshly synthesized [P_{8888}][oleate] IL.

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): δ = 0.88 (m, 14.99H), 1.26 (m, 57.49H), 1.48 (m, 15.91H), 1.61 (m, 1.70H), 1.99 (m, 3.38H), 2.16 (t, 1.71H), 2.40 (m, 6.46H), 5.33 (m, 1.37H).

It was observed that for the spectra from the IL applied in the continuous setup that all peaks were broadened due to the interaction of cobalt. In both spectra no peak around 1.59 and 2.17 ppm was observed, but it is assumed that these peaks are being overlapped by the peak at 1.47 and by the peaks at 1.98 and 2.32 ppm, respectively. Both spectra at time 60 min and 300 min look similar.

NMR spectra IL after being applied in the continuous metal extraction setup for 60 min

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): δ = 0.87 (15.00H), 1.27 (51.14H), 1.4 (14.46H), 1.99 (2.37H), 2.31 (6.37H), 5.33 (0.61H).

NMR spectra IL after being applied in the continuous metal extraction setup for 300 min

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): δ = 0.88 (15.00H), 1.27 (50.92H), 1.45 (19.32H), 2.01 (2.77H), 2.28 (5.40H), 5.35 (0.65H).

SI.6.4. Price calculations IL [P_{8888}][oleate]

Table SI.6.1. Price calculation of the IL [P_{8888}][oleate]

	lab scale	ton scale
P_{8888}Br	€ 72 per 100 gram by Iolitec	€ 28800 per ton[b]
	€ 720000 per ton	
oleic acid	€ 112,80 per 500 mL by Fischer	€ 1013,5 per ton[a]
	€ 112,80 per 445 g by Fischer	
	€ 0,253 per 1 g by Fischer	
	€ 253.000 per ton	
price ratio lab scale/ton scale		250
caustic soda (NaOH)		€ 546 per ton[a]
[a] price according to icis.com [b] price calculated via one tenth of the lab/ton price ratio for oleic acid, reason for the factor one tenth is that oleic acid can directly be extracted from olive oil, while P_{8888}Br still needs to be synthesized		
To synthesize 1 Kg of IL (reaction yield of 95%) we need:		
N_{8888}Br	770 g	€ 22,18
oleic acid	502 g	€ 0,51
NaOH	98 g	€ 0,02
price per Kg IL on a ton scale		€ 22,71
price per Kg IL, including manufacturing costs		€ 30,00
price per L IL (ρ = 0,89 $\mathrm{g{\cdot}mL^{-1}}$)		€ 33,71

SI.6.5. Economical analysis IL vs. IER

An economical analysis was performed for an ion-exchange resins (IER) system for the continuous metal removal of cobalt from an industrial waste stream from a paint industry producing on average 200 m^3/month wastewater or on average 278 $L{\cdot}h^{-1}$. Characteristics of the waste water can be found in Table SI.3.1.

Table SI.6.2. waste water characteristics of Binalood Paint Industries

Parameters	Mean	SD	Unit
pH	5.5	1.5	pH unit
BOD	252.5	20.9	$mg{\cdot}L^{-1}$
COD	610	32.47	$mg{\cdot}L^{-1}$
TSS	102.5	13.9	$mg{\cdot}L^{-1}$
TDS	3325	491.05	$mg{\cdot}L^{-1}$
EC	1750	217.3	$\mu S{\cdot}cm^{-1}$
Pb	5.4	1.3	$mg{\cdot}L^{-1}$
Co	1.15	0.26	$mg{\cdot}L^{-1}$
Cd	1.6	0.29	$mg{\cdot}L^{-1}$

BOD = biological oxygen demand, COD = chemical oxygen demand, TSS = total suspended solids, TDS = total dissolved solids, EC = electrical conductivity

Table SI.6.3. Economical analysis for an ion exchange resin system to capture cobalt from waste water presented in Table SI.6.2

Ion-exchange system				
construction				
Units	2 Parallel IE colums to ensure continuous treatment	cost/pcs	number	totals
column	PP/PE; 1,5 m high; 100 L volume	€ 2.000	2	€ 4.000
Pomps	0,28 m^3/hr	€ 1.500	2	€ 3.000
Salt storage and dosing	200 L container + dosing pump	€ 300	2	€ 600
Sensoring	conductivity	€ 1.500	1	€ 1.500
engineering		€ 20.000	1	€ 20.000
control & cabling		€ 7.000	1	€ 7.000
skidassambly		€ 2.500	1	€ 2.500
engineering		€ 4.000	1	€ 4.000

	sum			€ 42.600
Consumables		€/kg	consumed	price/h
Ion exchange resins	100 L column	€ 25	100	€ 2.500
Purolite® S924 (€50 /25kg)	with the assumption that 100 kg IER fills a 100L column	€/ltr		
brine/regeneration solution	Flush column with 200L brine (1M NaCl) after 10 h (€0,27 /kg NaCl)	€ 0,016	40 l/h	€ 0,64
Power	2x 0,5 kW (€0,09 /kWh)			€ 0,09
	Operation (€/h)			€ 0,73

Table SI.6.4. Economical analysis for a continuous metal extraction system based on the [P_{8888}][oleate] IL for the recovery of cobalt from waste water from the paint industry presented in Table SI.6.2.

IL system				
construction				
Units	Specifics	cost/pcs	number	totals
kolom	Same column as Ion-exhange systems, PP/PE	€ 2.000	2	€ 4.000
Mixing bath	50 L PP/PE	€ 500	2	€ 1.000
Pomps	0,28 m^3/hr	€ 1.500	5	€ 7.500
mixing	0,75 kW	€ 1.000	1	€ 1.000
IL storage and dosing	200 L 1 month, incl dosing pump incl cabinet	€ 2.000	1	€ 2.000
$Na_2C_2O_4$ storage and dosing	5 L 1 month, incl dosing pump incl cabinet	€ 1.000	1	€ 1.000
piping		€ 5.000	1	€ 5.000
sensoring	level, pH	€ 2.000	1	€ 2.000
control & cabling		€ 15.000	1	€ 15.000
skidassambly		€ 5.000	1	€ 5.000
engineering		€ 20.000	1	€ 20.000
IL/IONX	buffer container MDPE, 1,5 m^3; 5 hr buffer	€ 1.500	1	€ 1.500
	sum			€ 65.000

Consumables		€/ltr	Consumed	price/h
Startliquid IL	x L	€ 33,7	100	€ 3.370
IL	Depletion due to solubility loss (≤18 ppm assumption)	€ 33,7	0,010 kg IL/h	€ 0,31
$Na_2C_2O_4$	Price Oxalate (€2 /kg), 0,1 M stripping solution	€ 0,0268	278 l/h	€ 7,69
Power	5 x 0,5 kW (€0,09 /kWh)			€ 0,23
	Operation (€/h)			€ 8,23

Chapter 7

Combine electrospray with ionic liquids

This chapter is accepted for publication in journal of electrostatics as:

Dries Parmentier, Anna Rybałtowska, Jasper van Smeden, Maaike C. Kroon, Jan C. M. .Marijnissen, Luewton Lemos, Applying electrohydrodynamic atomization to enhance mass transfer of metal salts from an aqueous phase towards ionic liquids.

7.1. Introduction

Heavy metals are a common source of pollution in water. Their origin is rather diverse. While arsenic (As) normally originates from the oxidation of sulfide minerals like arsenopyrite, lead (Pb) has its origin normally from old metallic distribution and drainage systems and mine machinery maintenance yards. Cadmium (Cd), zinc (Zn), manganese (Mn) and iron (Fe) have their source from industrial processes and mercury (Hg) is normally dispersed from small scale (artisanal) mining.[1] Among them Cd is especially known by its high toxicity and as an environmental hazard.[2] Nowadays, it is mainly As that has been mentioned as a potential health risk for drinking water in many countries.[3–6]

Several techniques can be used to remove these metals from liquid effluents, e.g. precipitation, solvent extraction, ion exchange, adsorption, membrane filtration (micro, ultra, and nano), coagulation–flocculation, flotation and electrochemical methods.[7] Even though the list of suitable methods is large, the removal of such contaminants from wastewater streams below the standard limits is still a challenge.[8] The main limitations of the current methods are the high capital and/or operational expenditure and the high standards for influent quality.[9]

Among all current techniques, solvent extraction is commonly used for the separation and purification of metals.[10] It comprises basically a chemical extraction process, where an extractant agent is dispersed in a solution containing the contaminant using some form of energy, e.g. mixing or stirring. The removal process can be either an ion-exchange process, or liquid-liquid extraction with metal extractants. Examples of such extractants are di(2–ethylhexyl) phosphoric acid, tris(2–ethylhexyl)amine and liquid phosphine oxides dissolved in organic solvents such as kerosene or toluene.[11,12] This method is known by its high extraction efficiency, i.e. extraction efficiencies above 99% can be reached. However, it presents high operational costs due to the handling and disposal of the used solvents, which are normally highly toxic, flammable and/or volatile.

If assumed that the volatility of the organic solvents and the toxicity of the extractant and solvent are the main disadvantages of current chemical extraction processes, then finding "green" extractants", i.e. bio-degradable/non-toxic extractants, would represent a big improvement for this industry. Recently, the use of Ionic Liquids (IL) has been considered as a potential solution.[13–15]

ILs are known as substances entirely formed by anions and cations that melt at or below 100 °C.[16,17] The composition of an IL is a bulky organic cation combined with an inorganic or organic anion. The strong electrostatic interactions between the ions result in their characteristic properties, i.e. their negligible low vapour pressure at room temperature and the high chemical and electrochemical stability.[18] Moreover, other properties like solubility and viscosity can be modified by substituting different anions and cations.[19–24] As well as their application, i.e. selecting ions with functionalities that interact with metals results in ILs suitable for metal extraction.[25–27]

Currently, metal extraction with ILs is carried out using a mixer-settler configuration. This means that physical mixing of the IL with the aqueous metal solution is performed to enhance the contact between the extracting phase and the solution containing the contaminant.[28] In practice, any other technique which could create an enhanced interface with less energy would improve the system's efficiency. A good possibility is to modify this interface using electrical forces, i.e. exposing the liquids to a strong electric field.

A technique that uses such principle is electrohydrodynamic atomization (EHDA).[29–32] EHDA, or shortly electrospraying, is an atomization process, which implements electric stresses into the liquid leaving the nozzle. These stresses are inserted by creating a strong electric field in the breakup region by applying an electric potential between the nozzle and a counter electrode. For a certain nozzle-counter electrode configuration (defining the electrical field strength) and a specified liquid, different spraying modes can be obtained depending on the applied potential difference, and the liquid flow rate. This paper only considers low flow rates. For low flow rates ($\mu l \cdot h^{-1}$ – $mL \cdot h^{-1}$) the mode changes by increasing the potential from dripping via intermittent to cone-jet mode (Figure 7.3.). By further increasing the potential a multi-jet mode appears. If the electric field strength becomes too high, sparking can take place. In the cone-jet mode the shape of the liquid surface is transformed into a cone and from the apex of the cone a liquid jet emerges, which is much thinner than the nozzle diameter. The jet then breaks up in small, highly charged droplets (nm-µm), which can be monodisperse. Among many other applications, electrospraying is used for drug delivery,[33,34] in greenhouses,[35] and for controlled deposition.[36]

In EHDA the electric field is created by establishing an electric potential difference (Φ) between the nozzle and a counter electrode placed at a certain distance from the nozzle's tip. Various nozzle/counter electrode configurations can be used. The most known one is the nozzle/plate configuration, in which the counter electrode is a metallic plate placed below the nozzle tip.[36] Alternatively, configurations like coaxial cylindrical nozzles[37] and nozzle/ring[35] systems have also been successfully applied.

For a liquid with a high surface tension, such as water, the electric field necessary to overcome the surface tension stress and to transform the liquid surface into a stable cone, is so high that sparking happens before the cone formation can be reached. A possible way to overcome this problem is to use two coaxial nozzles in where the outer liquid is a well electrosprayable liquid and the inner one is the non-electrosprayable liquid.[38] This process is also known as "electro-coextrusion".[39] If this is done with a coaxial configuration, then also an extended specific contact area between the two liquid phases can be realized.

In this work a coaxial nozzle system was developed so that IL and salt solution can be simultaneously electrosprayed in the cone-jet mode, as shown in Figure 7.1. The combination of EHDA with ILs was to the best of the authors knowledge investigated for the first time to see whether it can be used to improve the selectivity and extraction efficiency of metals into the IL solution.

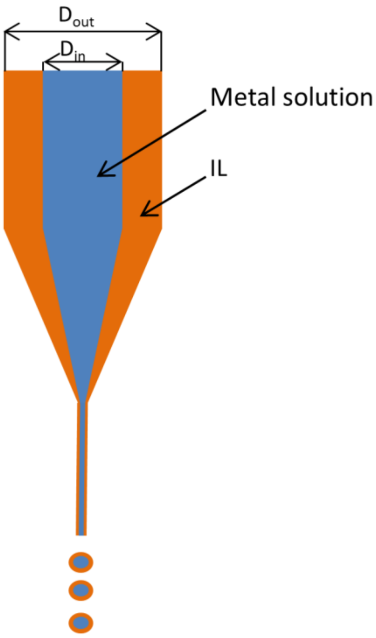


Fig 7.1. *Ideal cone-jet mode with the formation of encapsulated droplets*

7.2. Experiment and materials

Materials

The atomized liquids were an aqueous salt solution and the IL, i.e. tetraoctylammonium oleate ([N_{8888}][oleate]). The IL was selected because it is already known as an efficient selective metal extractant for transition metal ions from light metals.[40] Before using the IL, it was pre-saturated with water to decrease the viscosity and to facilitate electrospraying. The aqueous metal salt solution was prepared by dissolving 0.5 g of each salt ($MnCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, NaCl, $CaCl_2{\cdot}2H_2O$) in demineralised water. All chemicals were purchased from Sigma-Aldrich. MilliQ water (≥18.2 MΩ·cm) used throughout the synthesis was obtained by a Millipore Milli-Q® biocel, which used a Q-grade® column. The IL used in the experiments was synthesized using the same method as previously described and had a purity of ≥95% measured by ^{1}H NMR.[25]

The physical properties of both the IL and the aqueous metal salt solution were determined. (see Table 7.1) Density and viscosity were determined by an Anton Paar SVM 3000/G2 type stabinger, with an uncertainty of 0.0005 g.cm^{-3} for the density and 0.005 mPa·s for the viscosity at a fixed temperature which had an uncertainty of ±0.01 K. The water content was measured by a Karl-Fisher titrator (Mettler Toledo, model DL39) with a standard deviation of 100 ppm. Surface tensions were determined around room temperature with a Krűss K11 MK4 tensiometer using the plate method with a standard deviation of ± 0.03 mN·m^{-1}. Electrical conductivity was measured by a conductivity meter (WTW, TetraCon 325) with an uncertainty of 0.0001 S·m^{-1}.

Table 7.1. *Density (ρ), dynamic viscosity (η) at 20 ˚C, surface tension (σ) and electrical conductivity (K) of the metal solution and IL applied in this research compared to distilled water.*

Solution	*ρ(kg.m^{-3})*	*η* (mPa·s)	*σ* (N.m^{-1})	*K (μS·cm^{-1})*
[N$_{8888}$][oleate]	895	249	0,025 (±86*10^{-6}) at 21.7°C	9,1 at 23,7°C
Metal solution	1010	1.08	0,070 (±70*10^{-6}) at 25,2°C	2,3*10^{3} at 22,3°C
Dist. Water	1000	1.00	0,073 at 25°C	1.4 at 22,0°C

Experimental setup

In order to enhance the contact between the two liquids, i.e. to create an enlarged specific interfacial area, a coaxial nozzle configuration was used. Such configuration is widely applied in EHDA experiments to provide a liquid-liquid interface and to form encapsulated droplets.[41–43] For this research, a coaxial nozzle system as presented in Figure 7.2 was fabricated. The system structure was built with PP connectors from Emtechnik®. The concentricity of the nozzles was assured by attaching them to two connected DN 04/06 G /8 PP female connectors. Two different nozzles (EFD® precision) were used with the following dimensions: the external nozzle had 1.84 mm outer diameter (OD) and 1.54 mm inner diameter (ID), it was placed concentrically with the inner nozzle which had 0.72mm OD and 0.41 ID. First tests were done to stipulate which liquid configuration, i.e. internal nozzle and external nozzle liquid, would be the most appropriate for the experiments. As mentioned before, the best configuration to spray in the cone-jet mode was when the IL is the outer liquid and the aqueous metal salt solution is the inner liquid. To guarantee the controllability of the flow rate in each nozzle, the two liquids were pumped separately using two Aitecs® sp125 syringe pumps (see Figure 7.2). Due to the different densities (Table 7.1) a flow rate investigation had to be performed to identify which specific flow rates had to be used to avoid buoyancy inside the meniscus. Experiments have proven that a flow rate of 1 mL·h^{-1} for the aqueous metal salt solution (inner nozzle) and 1.2 mL·h^{-1} for the IL (outer nozzles) avoided buoyancy inside the meniscus and eventually allowed achieving a stable cone-jet mode. Therefore, all experiments were done using the previously mentioned flows.

The electrical connections were as follows: high voltage was applied to the counter electrode, i.e. a 14 mm copper ring placed 1 cm (distance h_1 represented in Figure 7.2) below the nozzles tips, while the nozzles were kept grounded. Preliminary experiments were done varying the electric potential between 0 and 6kV to check which modes would be obtained with which potentials as well as to observe whether a stable cone-jet mode could be achieved. After electrospraying, the solution was collected in a 15 mL centrifuge tube placed right under the nozzles (distance h_2 presented on Figure 7.2, h_2 = 0 cm)] and subsequently the aqueous phase was sent to be analyzed.

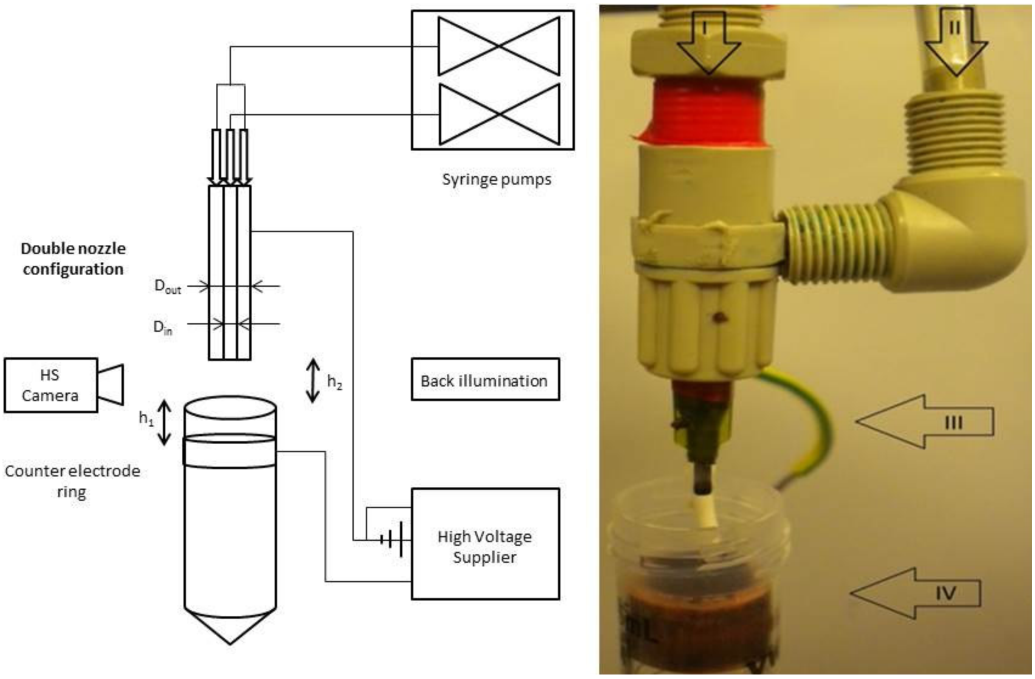


Figure 7.2. Schematic overview of the setup and a picture of the detailed coaxial configuration. The IL is injected through the inlet of the outer nozzle (II) and metal salt solution through the inlet of the inner nozzle (I). The electrical potential is applied between the outer nozzle (III) and the counter electrode ring (IV).

To allow the visualization of the spray, the identification of the spraying mode and the characterization of the produced droplets, i.e. droplet size and droplet size distribution, a high speed imaging system was utilized. It consisted of a high speed camera (Photron AS1) with a microscopic lens (Navitar J25 mm) and a back illumination (Dedo light could source) as represented in Figure 7.2.

In all experiments, the solutions were sprayed for one hour inside the plastic collector and then send to analysis (approximately 2.2 mL per tube). To be able to compare the performance of the electrospray system with conventional solvent extraction, solvent extraction experiments were also done using physical shaking (Heidolph multi reax multi-tube vortex mixer) with the same solutions. In these experiments the liquids (1 mL metal salt solution, 1.2mL IL) were brought into a 15 mL centrifuge cylinder and mixed on a vortex. Lastly, the extraction efficiency in a static extraction was also investigated. For that the two liquids (1 mL metal solution, 1.2mL IL) were placed in a 15 mL centrifuge cylinder without applying any physical mixing. In both cases (physical mixing and static), the water phase was separated from the IL after one hour, and analyzed regarding its metal content.

Analytical methods

Collected samples from electrospraying were, in a next step, placed in an Allegra TM X-12R centrifuge from Beckman Coulter for 5 min at 1500 rpm. Afterwards, the aqueous phases were analyzed for cations with a precisely inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) from Perkin Elmer, which used an optical emission spectrometer 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%.

Extraction efficiencies (E) were calculated by

$$E(\%) = \left(\frac{C_0 - C_1}{C_0}\right) x\ 100 \qquad (1)$$

where C_0 and C_1 are the total metal concentrations in the aqueous phase before and after the experiment. Measurements were performed in triplo. We present both the average values and the standard deviations.

7.3. Results and discussion

Electrospray mode identification.

Figure 7.3 is a representation of a preliminary investigation done to identify which modes would be established at different electric potentials. Electrospraying at different flow rates were also performed, but are not presented. The best flow rates of the 2 liquids (and so their ratio) were visually defined and optimized so that the inner liquid flows nicely inside the outer liquid in the cone-jet mode. Another point observed was the total duration of the experiments. As the chemical analysis required at least a volume of 1 mL of the aqueous phase, an initial inner nozzle flow of 1.0 $mL \cdot h^{-1}$ was defined to guarantee that the spraying time, per run, would be no longer than 1 hour. After optimization of the flow rates, 1.2 $mL \cdot h^{-1}$ for the IL, an electrospray mode analysis was performed by keeping flow rate configuration and nozzle to plate distance constant and applying different potentials to the counter electrode. Figure 7.3 is a representation of these results.

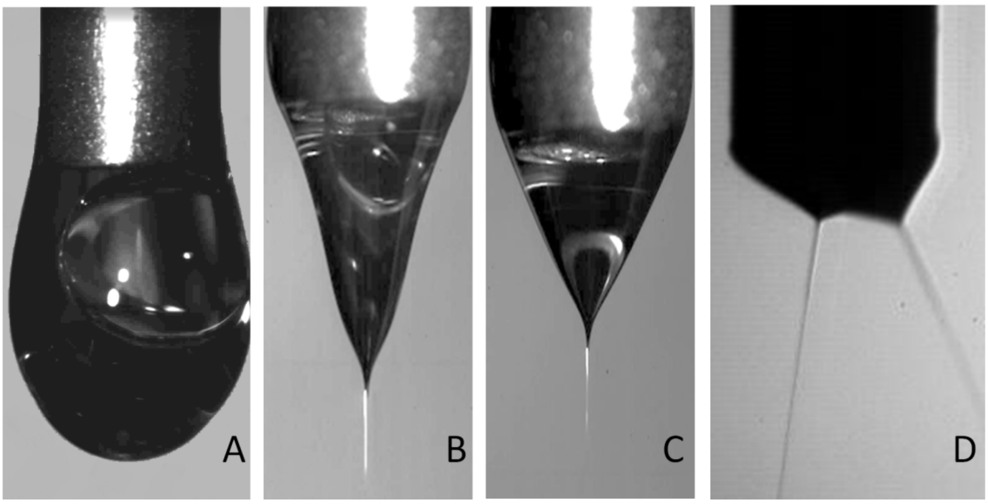


Figure 7.3. *Different modes observed with different applied potentials. From left to right: A) 0 kV; dripping, with the transparent droplet being the aqueous phase and the dark droplet being the IL, B) 4kV; intermittent cone-jet mode, C) 5 kV; cone-jet mode and D) 6 kV; multi-jet mode.*

The results in Figure 7.3 demonstrate that, even for the optimized flows, when no potential is applied, the water is not really encapsulated by the IL (Figure 7.3.A). It was observed that during this experiment at 0 kV, at some point the liquids switch position, i.e. the aqueous phase moves to the bottom of the growing droplet, a short time before the droplet falls from the nozzle. For potentials around 4 kV (Figure 7.3.B), an intermittent cone-jet mode could be observed and as can be seen, the shape of inner meniscus is slightly elongated following the shape of the outer meniscus. At 5kV, a stable cone-jet could be achieved (Figure 7.3.C). In this mode, an inner meniscus seems to occur, which is an initial indication of the formation of encapsulated droplets. Some disruptions of the Taylor cone were observed during this mode, most probably caused by the presence of space charges.[44] For potentials around and above 6kV a multi-jet mode could be observed (Figure 7.3.D).

Even though these first experiments have indicated the necessary configuration for the cone-jet mode, the extraction experiments were still performed with a range of different potentials to investigate the relation between extraction efficiency and applied potential, i.e. electrospray mode.

Extraction results

Figure 7.4 presents an overview of the extraction efficiency for the different metals when the electrospray is applied. A high extraction efficiency of cobalt (Co) and manganese (Mn) was noticed for 5 kV, which corresponds to the cone-jet mode. Negative extraction for calcium (Ca) and sodium (Na) during the experiment could be explained by the following reasons: (I) evaporation of water during electrospraying, (II) Na could be an impurity in the IL due to the use of NaOH during the synthesis of the IL, and (III) due to uncertainties of the analytical apparatus. The results obtained correlate with previous research, in which it was already observed that the IL, [N_{8888}][oleate], showed good extraction efficiencies for Co and Mn, but little extraction for Ca and no extraction for Na.[25,40]

Figure 7.5 shows the extraction efficiencies for each metal separately at the different potentials applied with the metal extraction efficiencies due to physical mixing and no mixing. The results demonstrate that Co and Mn have similar extraction efficiencies, but Ca and Na have much lower extraction efficiencies in case a high voltage is applied. This result is an improvement of the selectivity towards the valuable transition metals using EHDA. The separation factor for Co over Ca as well as Mn over Ca was 3.7 when applying physical mixing. For electrospraying at 5 kV a separation factor of 5.0 and 4.8 was observed for Co over Ca and for Mn over Ca, respectively.

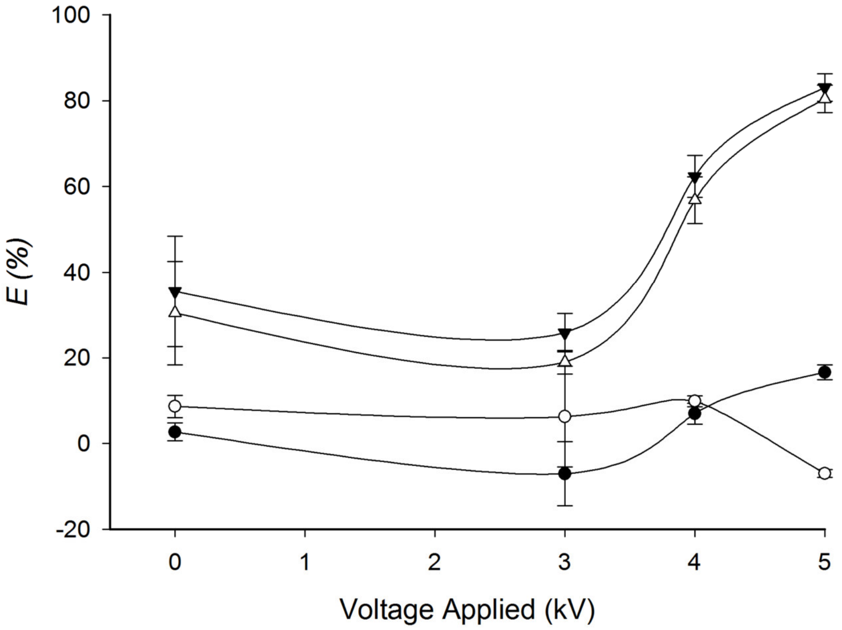


Figure 7.4. *Metal extraction for the elements Co (▼), Mn (△), Ca (●) and Na (○) by electrospraying an aqueous metal solution combined with IL through a coaxial nozzle as a function of the voltage applied.*

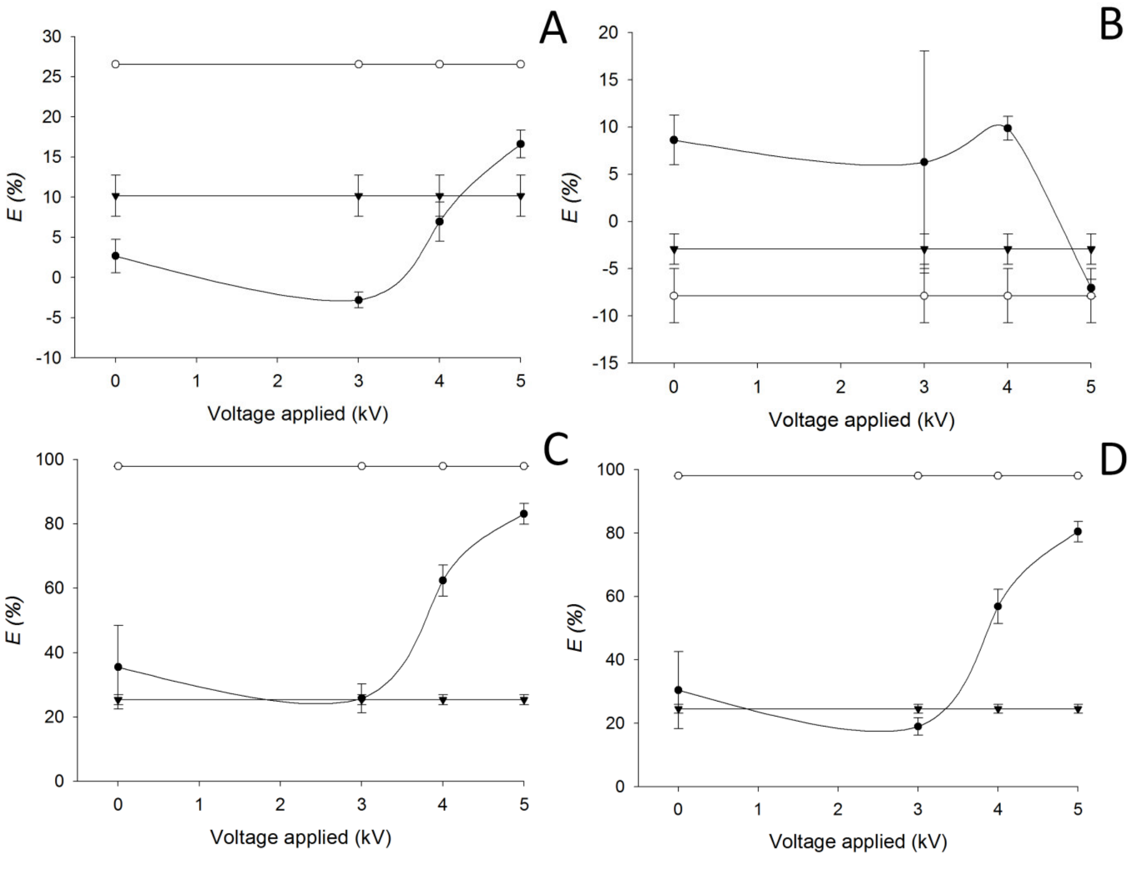


Figure 7.5. *Extraction efficiencies of Ca (A), Na (B), Co (C) and Mn (D) with the IL when a potential was applied (●) in comparison to physical mixing (○) and no mixing (▼).*

It seems that there are lower extraction efficiencies obtained at 3 kV voltage compared to 0 kV. However, these values were within the range of the standard deviation and it was difficult to confirm this trend. It was observed in the cone-jet mode (Figure 7.3.C) that the droplets size was 50-70 μm (in comparison with 2960 μm at 0 kV). Resulting in more contact area per unit volume between the two liquids in the jet and when they form encapsulated droplets, as suggested in Figure 7.1.

Unfortunately, it was not possible to visually verify the formation of encapsulated droplets. However, from the literature it is known that the encapsulation process of two liquids depends on: (1) whether the two liquids are immiscible, (2) whether the two liquids are mutually wettable, (3) whether the core liquid has a higher surface tension than the outer one.[45] All these requirements are met for the liquids used in the experiments, i.e. the IL is very hydrophobic and therefore not miscible with the water phase, the IL is for 10.8 wt% water saturated and from table 1 it can be observed that the aqueous phase has a higher absolute surface tension then the IL . Therefore, it can be assumed that the process will most probably form encapsulated droplets.

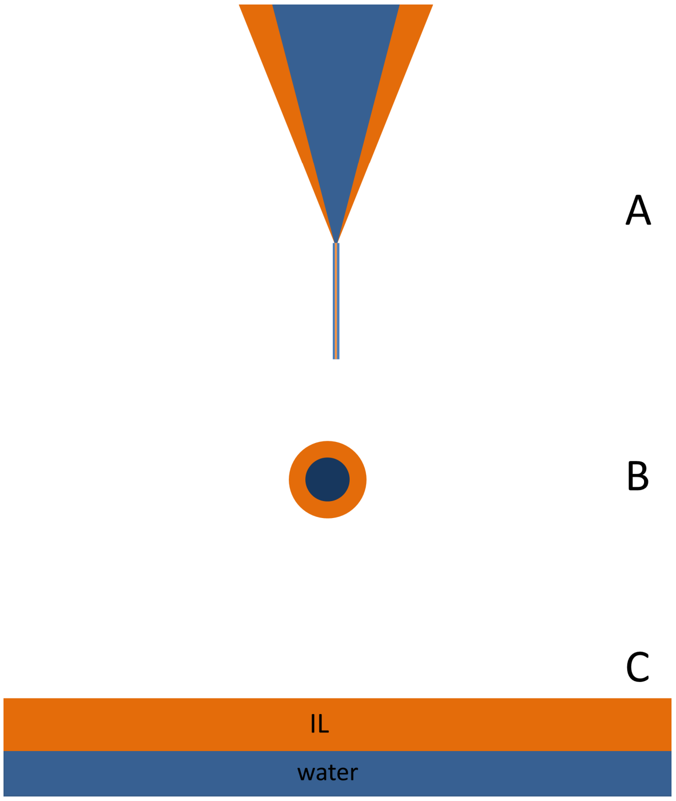


Figure 7.6. *Subdivision of the EHDA process with a hydrophobic IL and an aqueous metal solution. (not on scale) A) corresponds to the cone-jet, B) are the formed fine (whether or not encapsulated) droplets and C) represents the static extraction after collecting.*

To get an overall idea of enhancement of the extraction efficiency with EHDA, a systematic subdivision of the process should be taken into consideration, see Figure 7.6. The process can be divided in the formation of a cone-jet with a relatively long contact time between the 2 liquids (A), followed by the formation of fine droplets and in the ideal case encapsulated droplets (B) and after collecting, separation takes place and static extraction occurs on the interphase between the IL as well as the extraction between freshly sprayed water droplets that after collection still have to diffuse through the formed IL phase(C). To see the effect of electrospraying, the results from dripping the liquids out of the coaxial nozzle at 0 kV has to be compared with the results of electrospraying the liquids at 5 kV, see Figures 7.4 and 7.5. Dripping the two liquids at 0 kV is a process that can be subdivided in two processes. Droplet formation, in which the droplet is divided into an upper semi-sphere of IL and a lower water phase semi-sphere and static extraction, in which the two liquids separate out in two distinct phases inside a centrifuge tube due to gravity.

In the static extraction, the extraction rate of the metal ions is controlled only by the metal ion diffusion through the interphase in both liquids. Dripping the liquids at 0 kV compared to the static extraction, results already in a slight increase of metal extraction, except for Ca. This increase could be explained by the fact that in the dripping mode the liquids are already forced to be in close contact with each other what speeds up the metal extraction. Applying 5 kV resulted in a doubling of the metal extraction for Co and Mn. At this applied voltage an increase of metal extraction efficiency was also observed for Ca, but a negative extraction was observed for Na. Compared to dripping (0 kV), the cone-jet mode (5 kV) mode results into a fine jet and a spray of fine droplets, which increase the contact surface between the two liquids and result in a higher extraction.

It has to be reported that water was being evaporated during electrospraying when an electrical field was applied. A possible explanation for this observation is that not all the water is fully encapsulated by the IL or that water is evaporating from the IL. This also means that the actual extraction values for Co and Mn by electrospraying are probably higher than what is reported now.

Electospraying ILs in combination of aqueous samples could result into an interesting technique to purify samples just before analysis. The IL could then extract elements that disturb the analysis of the elements of interest in the aqueous sample or if the IL can be analyzed the enhanced separation factor towards the transition metals could results in a better qualitative analysis of traces of these metals. As electrospray is a flow technique with rather slow flow rates, this process will probably not be applicable in large scale industrial processes.

7.4. Conclusions

In this research, a coaxial nozzle configuration was applied to spray a hydrophobic IL together with an aqueous phase. It was found that the cone-jet mode could be obtained at 5 kV when the IL is the outer liquid with a flow rate of 1.2 $mL^{.}h^{-1}$ and the aqueous phase is the inner liquid with a flow rate of 1 $mL^{.}h^{-1}$. It could not be verified if the IL and water form encapsulated droplets, but it was proven that EHDA can enhance the metal extraction towards the IL (E_{Co} 83% and E_{Mn} 80%)close to the values of physical mixing (E_{Co} 98% and E_{Mn} 98%). Yet, higher separation factors were observed for the valuable transition metals compared to the light metals due to electrospraying. For example, the separation factor of Co over Ca was 5.0 when electrospraying was applied at 5 kV compared to 3.7 with physical mixing.

7.5. References

1 F. A. Armah, S. Obiri, D. O. Yawson, E. E. Onumah, G. T. Yengoh, E. K. A. Afrifa and J. O. Odoi, *J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng.*, 2010, **45**, 1804–1813.

2 F. Pinot, S. E. Kreps, M. Bachelet, P. Hainaut, M. Bakonyi and B. S. Polla, *Rev. Environ. Health*, 2000, **15**, 299–324.

3 K. G. Brown and G. L. Ross, *Regul. Toxicol. Pharmacol.*, 2002, **36**, 162–174.

4 A. H. Smith, C. Hopenhayn-Rich, M. N. Bates, H. M. Goeden, I. Hertz-Picciotto, H. M. Duggan, R. Wood, M. J. Kosnett and M. T. Smith, *Environ. Health Perspect.*, 1992, **97**, 259–267.

5 A. H. Smith, E. O. Lingas and M. Rahman, *Bull. World Health Organ.*, **78**, 1093–1103.

6 C. J. Chen, C. W. Chen, M. M. Wu and T. L. Kuo, *Br. J. Cancer*, 1992, **66**, 888–892.

7 F. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407–418.

8 J. E. Miller, *SAND 2003-0800, Unltd. Release*, 2003, 1–54.

9 M. Elimelech and W. A. Phillip, *Science*, 2011, **333**, 712–717.

10 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.

11 D. S. Flett, *J. Organomet. Chem.*, 2005, **690**, 2426–2438.

12 C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, *Ind. Eng. Chem.*, 1958, **50**, 1756–1762.

13 M. L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047–2063.

14 A. P. de los Ríos, F. J. Hernández-Fernández, L. J. Lozano, S. Sánchez, J. I. Moreno and C. Godínez, *J. Chem. Eng. Data*, 2010, **55**, 605–608.

15 H. Zhao, S. Xia and P. Ma, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1089–1096.

16 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.

17 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

18 R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792–793.

19 R. D. Rogers and G. A. Voth, *Acc. Chem. Res.*, 2007, **40**, 1077–1078.

20 L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water Res.*, 2011, **45**, 4601–4614.

21 J. F. Brennecke and E. J. Maginn, *AIChE J.*, 2001, **47**, 2384–2389.

22 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.

23 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.

24 A. Rout, J. Kotlarska, W. Dehaen and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16533–16541.

25 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2013, **15**, 205–209.

26 A. Rout and K. Binnemans, *Dalt. Trans.*, 2014, **43**, 1862–1872.

27 A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff and A. Wierzbicki, *Chem. Commun.*, 2001, 135–136.

28 G. M. Ritcey, *Tsinghua Sci. Technol.*, 2006, **11**, 137–152.

29 C. U. Yurteri, R. P. A. Hartman and J. C. M. Marijnissen, *KONA Powder Part. J.*, 2010, **28**, 91–115.

30 J. M. Grace and J. C. M. Marijnissen, *J. Aerosol Sci.*, 1994, **25**, 1005–1019.

31 D. P. H. Smith, *IEEE Trans. Ind. Appl.*, 1986, **IA-22**, 527–535.

32 I. Hayati, A. I. Bailey and T. F. Tadros, *Nature*, 1986, **319**, 41–43.

33 K. Tang and A. Gomez, *J. Aerosol Sci.*, 1994, **25**, 1237–1249.

34 J. C. M. Marijnissen, C. U. Yurteri, J. van Erven and T. Ciach, in *Nanoparticles in medicine and environment*, eds. J. C. Marijnissen and L. Gradon, Springer Netherlands, Dordrecht, 2010, pp. 39–57.

35 K. B. Geerse, J. C. M. Marijnissen, A. Kerssies, M. van der Staaij and B. Scarlett, *J. Aerosol Sci.*, 1999, **30**, S553–S554.

36 U. Stachewicz, C. U. Yurteri, J. Frits Dijksman and J. C. M. Marijnissen, *J. Aerosol Sci.*, 2010, **41**, 963–973.

37 V. R. Gundabala, N. Vilanova and A. Fernández-Nieves, *Phys. Rev. Lett.*, 2010, **105**, 154503.

38 M. Cloupeau and B. Prunet-Foch, *J. Aerosol Sci.*, 1994, **25**, 1021–1036.

39 M. A. Henderson and J. S. McIndoe, *Chem. Commun.*, 2006, 2872–2874.

40 D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans and M. C. Kroon, *Ind. Eng. Chem. Res.*, 2015, **54**, 5149–5158.

41 H. Chen, Y. Zhao, Y. Song and L. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 7800–7801.

42 W. Kim and S. S. Kim, *Anal. Chem.*, 2010, **82**, 4644–4647.

43 M. Orlu-Gul, A. A. Topcu, T. Shams, S. Mahalingam and M. Edirisinghe, *Curr. Opin. Pharmacol.*, 2014, **18**, 28–34.

44 L. L. F. Agostinho, E. C. Fuchs, S. J. Metz, C. U. Yurteri and J. C. M. Marijnissen, *Phys. Rev. E*, 2011, **84**, 026317.

45 G. Langer and G. Yamate, J. Colloid Interface Sci., 1969, 29, 450–455.

Chapter 8

Ionic liquids as concentrate phase in the electrodialysis process

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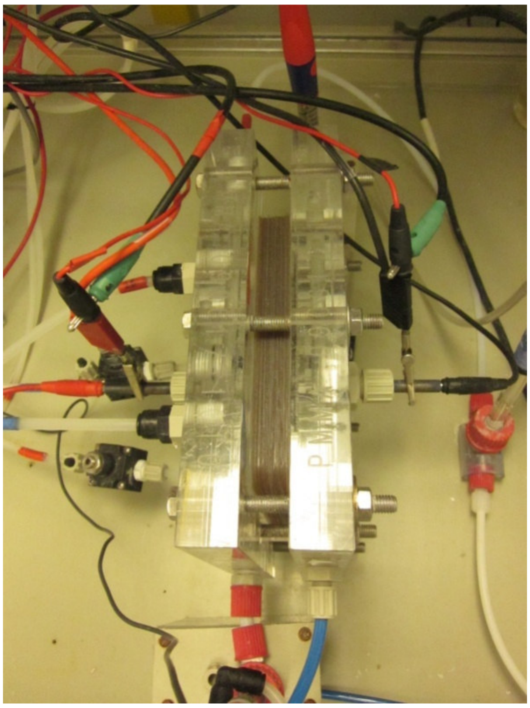

This chapter is submitted to Separation and Purification Technology as:

Dries Parmentier, Oane H. Galama, Małgorzata Nowak, Sybrand J. Metz and Maaike C. Kroon, Electrodialysis with ionic liquids: Selective metal extraction and minimized water transport

8.1. Introduction

Electrodialysis (ED) is a separation technique, which was discovered in 1890.[1] At present, ED is mainly applied for brackish water desalination and for treating industrial process water.[2] In this technique, cation exchange membranes (CEMs) are alternately arranged with anion exchange membranes (AEMs),while a direct voltage is applied to provide a current.[3,4] As a result of the applied potential difference between the electrodes, the dissolved cations migrate towards the negatively charged cathode, while the anions migrate in the direction of the positively charged anode. Positively charged ions permeate through the negatively charged CEMs, while being mainly retained by the positively charged AEMs. Vice versa, negatively charged ions permeate through the positively charged AEMs and are mostly retained by the CEMs.[5] This selective ion transport results in the formation of a diluate stream (low ion concentration) and a concentrate stream (high ion concentration), as shown in Figure 8.1.

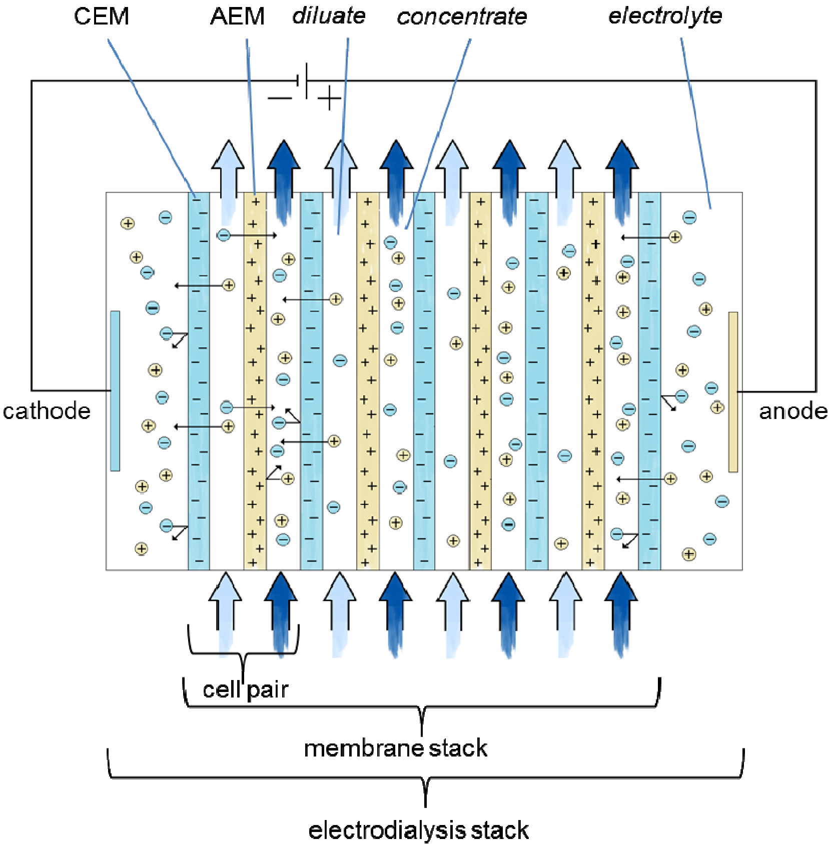

Figure 8.1. *Schematic representation of an electrodialysis stack, in which AEM represent the anion exchange membranes and CEM the cation exchange membranes. Anions are depicted with an encircled negative sign and cations by an encircled positive sign.*[6]

Although ED has a number of advantages over other desalination techniques, e.g. high scaling and fouling resistance, it also has disadvantages leading to limitations in its applicability.[7] For instance, the applicability of ED for metal recovery is limited due to transport of water from the diluate to the concentrate by osmosis and electro-osmosis.[8,9] Osmotic (or free) water transport takes place due to a difference in osmotic pressure, which is initiated by the difference in salt concentrations on each side of the membrane.[10] The larger the driving force (concentration difference), the larger the osmotic pressure difference and consequently the osmotic water transport. Electro-osmosis describes the water transport through the membrane that is related to the water in the hydration shell of the permeating ions.[11] The size of the electro-osmotic flux is therefore proportional to the ion flux and highly influenced by the type of membranes applied.[12] In ED, electro-osmosis and osmosis are unavoidable and limit the maximum obtainable concentration of ions in the concentrate stream.[6] Water transport through the membranes could be reduced by applying a strong hydrophobic medium in the ED concentrate channels. In this work, a hydrophobic ionic liquid (IL) that can stabilize metals will be tested as a hydrophobic medium for the first time.

ILs are defined as substances entirely composed of anions and cations, with a melting temperature at or below 100°C.[13,14] Typically, an IL consists of a bulky organic cation combined with an inorganic or organic anion.[15] Currently, one of the industrial applications of ILs focuses on liquid – liquid extraction.[16] Their negligible vapour pressure and non-flammability make this class of solvents very attractive for the replacement of volatile organic solvents that are commonly applied in biphasic extraction systems.[17] Another advantage of ILs is that they can be designed to extracted specific metals.[17–19] However, the usage of ILs for extraction processes is limited due to the high cost price of ILs, their relatively high viscosity which result in slow extraction rates and the risk of contaminating the water phase with ions from the IL.[20,21]

Combining ED with hydrophobic metal selective ILs could overcome some of the limitations of both processes: 1) water transport in the ED process can be reduced, 2) selective metal extraction can be achieved, while 3) at the same time the risk of polluting the water phase with ions from the IL is minimized by applying a physical barrier between the IL and the water phase. Synthesis and/or purification of an IL from an aqueous phase by ED has been described previously,[22–25] but to the best of our knowledge, an ED process in which a hydrophobic metal selective IL is applied as concentrate phase for selective metal extraction has not been reported in literature. Therefore, the purpose of this study is to investigate the applicability of introducing the low-viscous metal selective IL tetraoctylphosphonium oleate

([P_{8888}][oleate]) as the concentrate medium in an ED stack. This IL (Figure 8.2) was chosen because of its highly selective extractability towards transition metal salts.[15]

8.2. Experimental

Ionic liquid and materials

The IL [P_{8888}][oleate] was synthesized as described in detail by Parmentier *et al.*[26] Cobalt (II) chloride hexahydrate (99%), sodium chloride (≥99%), lithium chloride (≥99%) and nitric acid (68%) were delivered by Sigma-Aldrich (Zwijndrecht, Belgium). Milli-Q water (≥18 MΩ·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.

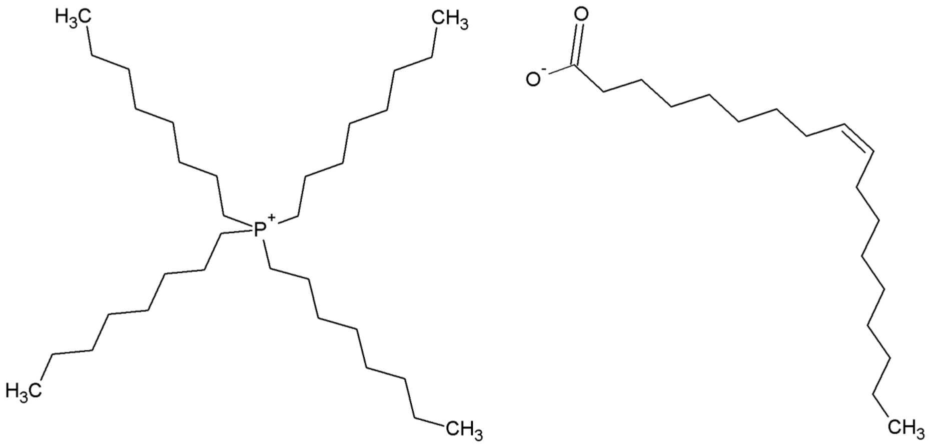

Figure 8.2. *Structure of [P_{8888}][oleate].*

Electrodialysis

The ED experiments were performed with an ED stack, consisting of ten repeating cell pairs. Each cell pair was built from two different ion exchange membranes: a CEM (Neosepta CMX, Tokuama Co., Japan) and an AEM (Neosepta AMX, Tokuama Co., Japan). In order to create flow channels for the concentrate and diluate streams, silicone gaskets (thickness 500±20 μm) containing a woven PET fabric spacer (Nitex 06 – 700/53 Sefar, Switzerland) were used to separate the membranes. The final cell pair of the membrane stack was closed by an additional CEM. Each membrane had an active area of 104 cm^2. Both square electrodes (cathode and anode) were placed facing each other on opposite sides of the stack. A titanium electrode (mesh 1.7, area 96.04 cm^2) coated with a mixed metal oxide layer (Magneto Special Anodes BV, The Netherlands) was used as an anode. For the cathode a titanium electrode (mesh 1.7, area 96.04 cm^2) with a 50 g/cm^2 platinum coating was applied (Magneto Special

Anodes BV, The Netherlands). As an electrolyte (electrode rinse medium) a 0.5 M sodium chloride solution was applied. This fluid was not circulated in the system, but the anolyte and catholyte were mixed, degasified and disposed.

The experiments were performed in a recirculation batch mode, as also described by Galama *et al.*[6] The diluate phase had a concentration of 4.0 $g{\cdot}L^{-1}$ $CoCl_2$ and 2.0 $g{\cdot}L^{-1}$ NaCl, and the concentrate phase was either a LiCl reference solution (0.021 $g{\cdot}L^{-1}$) or the IL. The reference solution had the same conductivity as the IL phase (~50 $\mu S{\cdot}cm^{-1}$) The IL phase was water saturated before use to lower its viscosity[26], and as a consequence to enhance salt transport through the concentrate channels. Initial volumes of the applied solutions were equal to 0.5 ± 0.01 L. Two different experiments were performed: 1) the initial concentrate is a LiCl solution and 2) the initial concentrate is a $[P_{8888}]$[oleate] IL. In both cases the initial diluate solution is the $CoCl_2$ / NaCl solution as described earlier.

The conductivity and the temperature of the diluate and concentrate were constantly monitored in line by four conductivity probes (Oakton, EW-35607-51, $\kappa = 10$), placed in the inflow and outflow of these two streams. The probes were connected to a data logger (Memograph M RSG40, Endress+Hauser) via a transmitter box (alpha cond 500, Eutech Instruments). The membrane stack voltage was measured by Ag/AgCl reference electrodes (QM711X, QIS) placed at the inlet of the anolyte and catholyte. A direct current (DC) with a current density of 20 A/m^2 was applied by a power supply (SM70–AR–24 Delta Elektronika).

To investigate the ion transport, samples of the diluate and concentrate were collected at defined time intervals (t=0, t=3, t=9, t=15, t=21, t=27, and t=33 min). The sample volume was approximately 4 mL. Before each sampling, the system was left to run without applied current for 1 min, in order to flush the system and remove the vertical concentration gradient in the stack that exists between inflow and outflow of the flow channels. The experiments were stopped after 33 min.

Sample analysis

First, a microwave assisted acid digestion had to be performed to be able to analyze the metal concentration in the IL phase. For this procedure, 0.2 g of the organic sample was placed in a fluorocarbon polymer microwave digestion tube with 4 mL of concentrated nitric acid and 5.8 mL of MilliQ water. The digestion tubes were sealed and heated in the microwave unit for 30 min at 180 °C and cooled afterwards before further diluting with a 3% nitric acid solution.

The aqueous phases of the diluate and concentrate samples were then analysed by an inductively coupled plasma (ICP) to determine the cation concentrations. A Perkin Elmer ICP was utilized, 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 µg/L and an uncertainty of 2%. The extraction percentage (*%E*) in case of equal volumes of the aqueous and organic phase can be calculated by

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

Osmotic water transport

Investigation of the osmotic water transport was performed using a modified PMMA diffusion cell (Figure 8.3.). The cell consisted of two 100 mL volume compartments, separated by a CEM (Neosepta CMX, Tokuama Co., Japan). The CMX was used for these experiments because it was shown to have slightly higher water content then the AMX membranes.[5] The interfacial membrane area was equal to 12.56 cm^2. In order to prevent leakage from compartment A to compartment B, the membrane was inserted between two PMMA o-rings with a Teflon support. The compartments were continuously stirred with magnetic stirrers to avoid concentration differences within each compartment. Water transport was measured by observing the change of the liquid level in two capillary pipettes that were connected to the cell compartment as shown in Figure 8.3.

Two experiments were performed to investigate the magnitude of the osmotic water transport. Duration of both experiments was 48h. Compartment A contained the $CoCl_2$ / NaCl initial diluate solution in both experiments. Compartment B contained MilliQ water in the first experiment and [P_{8888}][oleate] IL in the second experiment. The osmotic flux, J_w, was calculated according to equation 2:

$$J_w = {}^{V}\!/_{(A \cdot t)} \tag{2}$$

in which V (L) stands for the change in volume, A (m^2) is equal to the membrane surface area and t (h) is the time of the experiment.

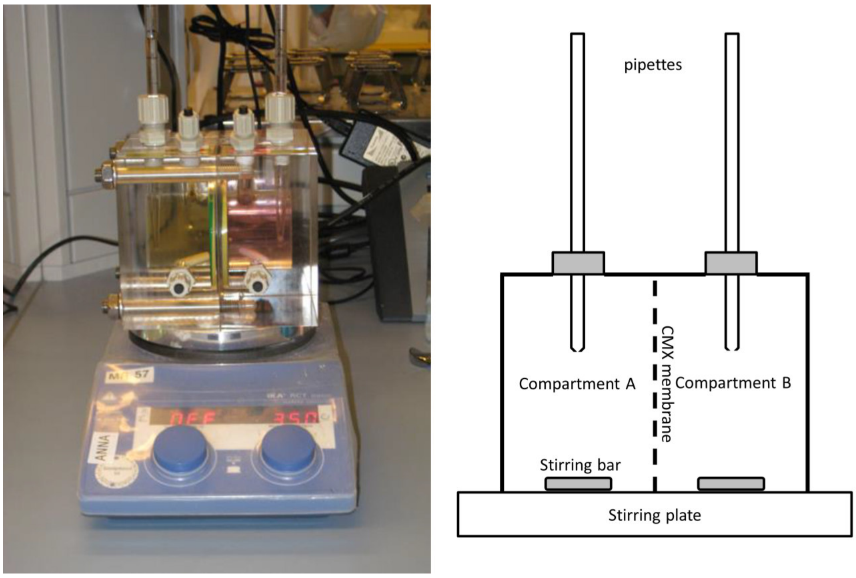

Figure 8.3. *Photo of the modified diffusion cell (left) and the schematic representation (right).*

8.3. Results and discussion

ED process

Figure 8.4 shows the samples that were taken from the IL concentrate and diluate streams during the ED process. In both experiments, whether the concentrate side was initially LiCl or IL, a colour change was observed for the diluate phase from transparent pinkish towards colourless due to the removal of cobalt. The LiCl concentrate changed from colourless to pinkish, while the IL concentrate showed a strong colour change from slightly yellow towards dark blue.

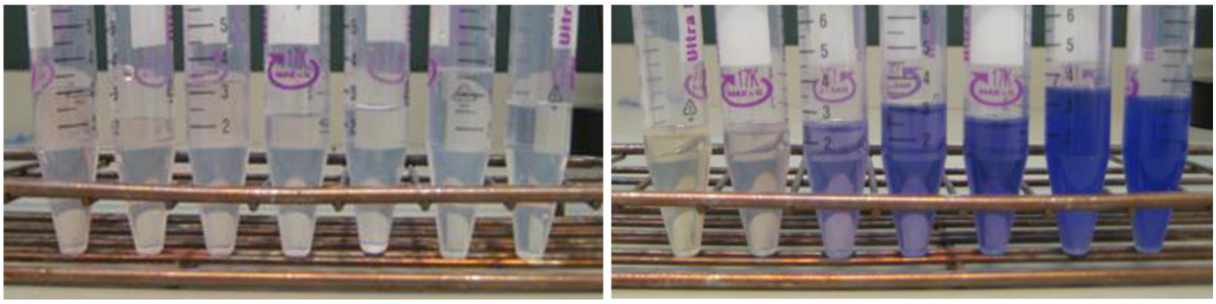

Figure 8.4. *Left: colour change from left to right of the diluate during the ED experiment from slightly pink towards colourless due to the removal of cobalt. Right: colour change from left to right observed in the IL concentrate due to the uptake op cobalt during the ED experiment.*

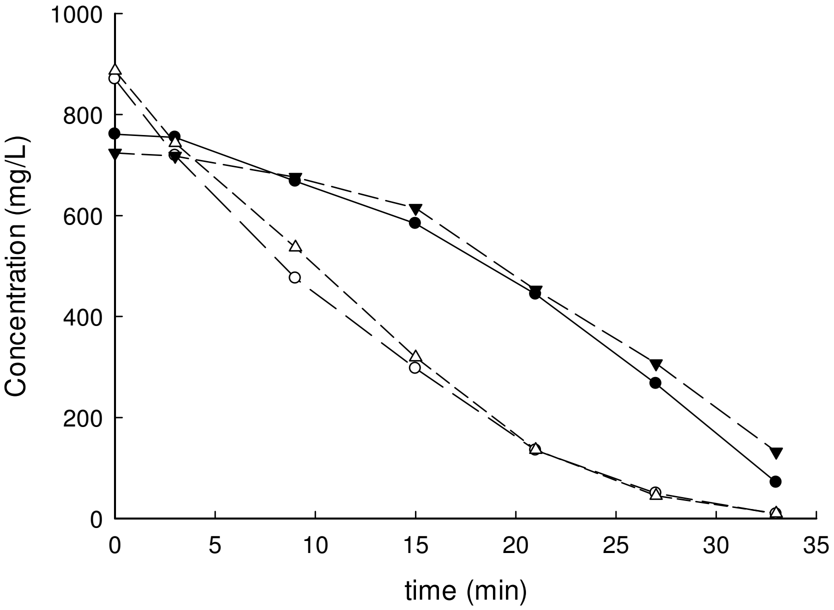

Figure 8.5. *Cobalt (○) and sodium (●) concentration changes in the diluate during the ED experiment with application of an aqueous LiCl phase as a reference as the concentrate and the cobalt (Δ) and sodium (▼) concentration changes when an IL is applied in the concentrate channels.*

Figure 8.5 shows the concentrations of cations presented in the diluate compartment with LiCl or IL in the concentrate compartment. In both cases a rapid decrease of cobalt concentration occurred in the diluate, while the initial decrease of the sodium concentration was slower. The reason for this phenomenon is that the experiment was performed at a low applied current density (20 A/m^2). This makes that concentration polarization effects are small, which favours the transport of divalent ions, and leads to a higher selectivity towards divalent ions.[27] Although the transition metal selective IL [P_{8888}][oleate] was introduced in the second experiment as a concentrate medium, it did not significantly contribute to any concentration profile changes at the diluate stream. This is a consequence of the mechanism of ED. Because the organic phase did not mix with the diluate, it did not change the physical principles of the performed ED. As a consequence, the selectivity of the IL towards certain ions did not contribute to the final concentration of ions in the diluate during the ED process, but this still depends on the applied electrical field. This finding of unchanged membrane selectivity also suggests that the membranes did not take up the IL, which is also not expected as the used membranes are hydrophilic.[28]

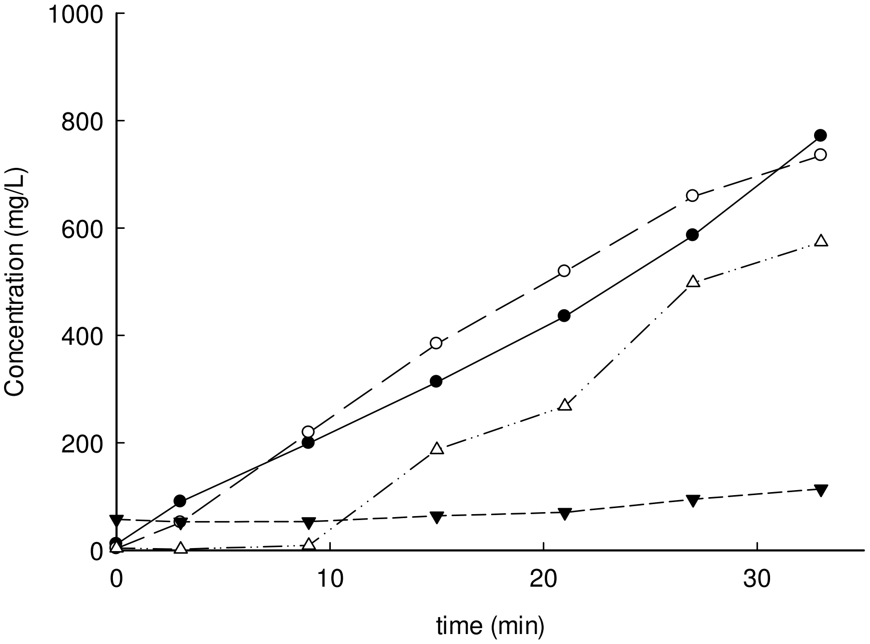

Figure 8.6. *Cobalt (○) and sodium (●) concentration changes in the concentrate during the ED experiment with application of an aqueous LiCl phase as a reference and the cobalt (Δ) and sodium (▼) concentration when the IL in the concentrate channels.*

Significant influence due to the presence of the IL is observed, however, for the metal concentrations of the concentrate stream (Figure 8.6). No significant difference in ion transport is observed between cobalt and sodium in the concentrate phase when the LiCl solution is applied, even though a faster removal for cobalt was observed in the diluate phase (Figure 8.5). Possible reason is that the transport rate of the divalent cobalt ions through the membrane is slower due to their bigger size and higher valence compared to the sodium ions.

A lower concentration of cobalt is observed in the IL when it is applied as concentrate phase instead of LiCl. Main reason for the reduced concentration of cobalt is the occurrence of cobalt (II) oxide precipitates on the outer membrane surface and cathode (Figure 8.7). Formation of cobalt precipitates in the cathode compartment demonstrate that cobalt is effectively transported out of the stack, reducing the maximum recovery. On larger scale the relative size of this effect will diminish, as the number of cell pairs will be much larger. An option to avoid leakage of cobalt to the catholyte could be to change the membrane arrangement such that the outer membranes are AEM instead of CEM. Another reason for the reduced concentration of cobalt could be that the current measurement method of ions in IL is not completely reliable due to the extra destruction step needed. Reason to doubt about this method was that a gradual uptake of cobalt was visually observed in Figure 8.4., while the concentration profile (Figure 8.6) showed that cobalt extraction started only after 9 min.

When the IL is used, the concentration profile of sodium stays low (52-114 mg·L^{-1}) and appears to be approximately constant. It is assumed that this result is due to the selectivity of the IL [P$_{8888}$][oleate] towards cobalt versus sodium. However, the fate of the removed sodium ions is still an important discussion point. A probable explanation for the removal of sodium out of the diluate phase without increasing the sodium content in the concentrate phase is that the sodium is transported to the electrolyte solution between the outer membranes and the electrodes. However, a much lower removal rate of the sodium ions from the diluate is then expected for a system with IL compared to the blank ED system. Removal rates were found to be similar and therefore, this explanation is unlikely to be true. Another option is that it precipitates on the membrane surface as the solubility of sodium in the IL phase is very small. However, sodium precipitation was not visually observed, and the solubility of sodium in the water phase, which is present in the IL phase, should be sufficient to avoid precipitation. The water volume in the IL when fully saturated is 10.8%,[26] indicating that 0.5 L of the IL solution contains 54 mL of water. Water has a maximum solubility of 360 g NaCl·L^{-1}, this results that the water in the IL should be able to dissolve maximum 13 g of NaCl, which is much more than the concentration in the diluate (2 g·L^{-1} NaCl in 0.5 L). It is more likely that the analysis of the ions in the IL phase was not entirely suitable and needs to be determined by another analysis.

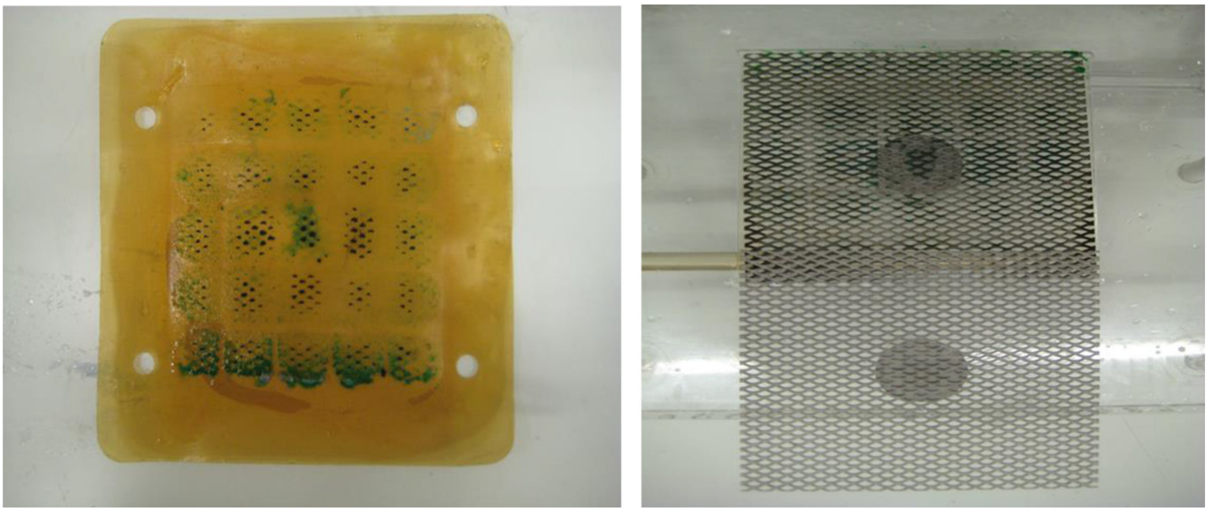

Figure 8.7. *Cobalt(II) oxide precipitation on the outer CMX surface (left picture), and on the platinised cathode (right picture, upper electrode), compared with clean cathode (right picture, lower electrode).*

Osmotic water transport

An important aspect for the ED performance is the water transport by osmosis and electro-osmosis from the diluate to the concentrate.[6] No changes in volume were observed for the diluate or concentrate phase when the LiCl or IL were applied, indicating no significant water transport occurred during the experiment. Therefore, an additional experiment was performed to investigate the water transport, because no changes in volumes were observed during the performed ED experiments. This osmotic water transport experiment was performed in two steps. For the first experiment, the diffusion cell contained the diluate solution at one side of the membrane and MilliQ water on the other side, while for the second experiment the MilliQ water was replaced with the IL, $[P_{8888}]$[oleate]. The calculated osmotic fluxes after 48 h were +0.007 $L/m^{2}\cdot h$ when MilliQ water was applied and -0.017 $L/m^{2}\cdot h$ when the IL was applied.

The water transport in the experiment involving the IL occurs slightly faster in comparison to MilliQ water. Moreover, in this case water is transported from the diluate solution towards the IL, while in the experiment with MilliQ water the water flow is in the opposite direction. This phenomenon can be easily explained by the differences between the structures of the solutions used in the investigations. ILs are organic solvents entirely made of ions,[29] resulting in a high amount of charged species present in the liquid and thus a large osmotic pressure. This osmotic pressure results then into a water uptake from the metal solution, which contains a low amount of ions in comparison to the IL, into the IL. Yet, once the IL is completely water saturated there is no driving force anymore for additional water uptake. During the experiment the formation of a separated water phase in the IL compartment did not occur. This leads to the assumption that the $[P_{8888}]$[oleate] was not fully saturated with water before the start of the osmotic water transport experiment, even though the IL was left overnight with an excess of water before usage to make sure that it was fully water saturated. On the other hand, it was also observed that at the interface with the CMX membrane the IL changed color due to the uptake of cobalt. The increase in volume could then be related due to the uptake of water by these metals in their hydration shell. Nevertheless, it can be concluded that the osmotic flux when the $[P_{8888}]$[oleate] IL is applied is very low.

In theory, the high hydrophobicity of the IL should avoid the problem related with diluting the concentrate stream. As the water and organic phases does not mix, the water transport does not affect the concentration of ions in the IL concentrate phase. Therefore, the combination of hydrophobic metal selective ILs with ED result in a process that next to the desalination of water also results in the selective concentration of transition metals in the IL.

8.4. Conclusions

This research shows that the ED process can be operated with a hydrophobic metal selective IL as concentrate phase. The removal ratio of ions out of the diluate phase depends on the ED process and the uptake of ions in the concentrate phase depends on the selectivity of the IL. During the ED experiment, no water transport was observed and no leakage of IL from the concentrate phase to the water phase occurred. It was concluded that the combination of hydrophobic metal selective ILs with ED result in a process that can both desalinate water and concentrate specific transition metals.

8.5. References

1 S. Itoi, I. Nakamura and T. Kawahara, *Desalination*, 1980, **32**, 383–389.

2 V. A. Shaposhnik and K. Kesore, *J. Memb. Sci.*, 1997, **136**, 35–39.

3 H. Strathmann, *Ion-Exchange Membrane Separation Processes | 978-0-444-50236-0 | Elsevier*, Elsevier B.V., Amsterdam, 2004.

4 J. R. Wilson, *Demineralization by electrodialysis*, Butterworths Scientific Publications, 1960.

5 A. H. Galama, J. W. Post, M. A. Cohen Stuart and P. M. Biesheuvel, *J. Memb. Sci.*, 2013, **442**, 131–139.

6 A. H. Galama, M. Saakes, H. Bruning, H. H. M. Rijnaarts and J. W. Post, *Desalination*, 2014, **342**, 61–69.

7 H. Strathmann, *Desalination*, 2010, **264**, 268–288.

8 W. Pronk, M. Biebow and M. Boller, *Environ. Sci. Technol.*, 2006, **40**, 2414–2420.

9 R. P. Tison and Y. M. Mikhail, *J. Memb. Sci.*, 1982, **11**, 147–156.

10 A. H. Galama, J. W. Post, H. V. M. Hamelers, V. V Nikonenko and P. M. Biesheuvel, *J. Membr. Sci. Res.*, 2015.

11 C. Jiang, Q. Wang, Y. Li, Y. Wang and T. Xu, *Desalination*, 2015, **365**, 204–212.

12 N. Berezina, N. Gnusin, O. Dyomina and S. Timofeyev, *J. Memb. Sci.*, 1994, **86**, 207–229.

13 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

14 J. S. Wilkes, *Green Chem.*, 2002, **4**, 73–80.

15 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2012.

16 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.

17 A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff and A. Wierzbicki, *Chem. Commun.*, 2001, 135–136.

18 A. Rout, J. Kotlarska, W. Dehaen and K. Binnemans, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16533–16541.

19 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.

20 M. L. Dietz, *Sep. Sci. Technol.*, 2006, **41**, 2047–2063.

21 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

22 S. Himmler, A. König and P. Wasserscheid, *Green Chem.*, 2007, **9**, 935.

23 H. Li, H. Meng, C. Li and L. Li, *Desalination*, 2009, **245**, 349–356.

24 X. Wang, Y. Nie, X. Zhang, S. Zhang and J. Li, *Desalination*, 2012, **285**, 205–212.

25 K. Haerens, P. De Vreese, E. Matthijs, L. Pinoy, K. Binnemans and B. Van der Bruggen, *Sep. Purif. Technol.*, 2012, **97**, 90–95.

26 D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans and M. C. Kroon, *Ind. Eng. Chem. Res.*, 2015, **54**, 5149–5158.

27 A. H. Galama, G. Daubaras, O. S. Burheim, H. H. M. Rijnaarts and J. W. Post, *J. Memb. Sci.*, 2014, **452**, 219–228.

28 E. Güler, W. van Baak, M. Saakes and K. Nijmeijer, *J. Memb. Sci.*, 2014, **455**, 254–270.

29 J. G. Huddleston and R. D. Rogers, *Chem. Commun.*, 1998, 1765–1766.

Chapter 9

Selective sodium extraction with ionic liquids

This chapter was submitted to “ Solvent Extraction & Ion Exchange” as:

Dries Parmentier, Magali Lavenas, Enver Güler, Sybrand J. Metz and Maaike C. Kroon, Selective removal of sodium from alkali-metal solutions with tetraoctylammonium monensin.

9.1. Introduction

A high concentration of sodium in water limits its use for drinking water.[1–3] Also, reuse of the irrigation water in greenhouses is often limited by the accumulation of sodium salts. Nowadays, this irrigation water, still containing valuable plant nutrients, is often discharged to the environment as a brine stream.[4,5] Industrial water containing to much sodium on the other hand leads to corrosion problems of metal parts in pilots.[6]

Therefore, selective removal of sodium from brackish and sea water could lead to the easier availability of drinking water. Reuse of water and nutrients would also be enhanced when sodium could be selectively removed from irrigation water. And industrial plants could be protected from corrosion if the process water contained less sodium. However, up to now there is still no cost-effective industrial technology that can selectively remove sodium.

Ionic liquids (ILs) are organic solvents consisting entirely of ions. The strong electrostatic forces in these solvents result in a low volatility and low flammability. Due to these properties, ILs were selected as ideal replacements for volatile organic solvents, which are common in industry.[7–13] Furthermore, by selecting the right organic ions to compose the IL, one can obtain an IL that is ideal for metal extraction. It has already been demonstrated that some of them show excellent efficiencies for the extraction of transition and rare earth metals from aqueous phases, but less attention has been given to the extraction of alkali metals.[14–20] Attempts to facilitate alkali metal extraction have been done by adding crown ethers, aza-crown ethers and calixarenes to hydrophobic ILs.[21–27]Unfortunately, analysis of the extraction mechanism showed that in these cases alkali metal extraction was based on ion-exchange, resulting in the loss of the cation of the IL into the aqueous phase, which is not sustainable.[28]

Task-specific ionic liquids (TSILs) for metal extraction were developed to avoid ion-exchange processes, and to avoid the leakage of the cation of the ILs into the aqueous phases during metal extraction.[29–33] In these TSILs a metal binding functionality was incorporated into the cation or anion. TSILs for alkali metal extraction have mostly ether functionalities built in.[34,35]

An alternative organic compound, which has specific affinity towards sodium, is monensin.[36–38] Its structure is related to crown-ethers in which a sodium ion can be nicely encircled. Monensin and its ester derivatives have already been tested to make sodium selective membranes, but an IL with monensin as anion has to the best of the authors knowledge not been reported before.

In this research, a TSIL was developed using monesin as an anion. This TSIL was afterwards tested for selective sodium removal from a mixed salt solution containing different alkali metals (lithium, sodium and potassium). The performance of the TSIL develop was compared to sodium monensin and 2-hydroxymethyl-15-crown-5. Afterwards, additional tests were performed to test the regeneration and reuse of this extractant.

9.2. Experimental

Materials

The extractant tetraoctylammonium monensin ([N_{8888}][monensin]) applied in this research was synthesized with reagents purchased from Sigma-Aldrich: sodium monensin (90-95%) and tetraoctylammonium chloride (≥97%). All salts applied in this research had a purity above >98%. Magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$) and 2-hydroxymethyl-15-crown-5 (95%) were also delivered by Sigma-Aldrich. Toluene, sodium chloride (NaCl), calcium(II) chloride dihydrate ($CaCl_2{\cdot}2H_2O$) and potassium chloride (KCl) were obtained from VWR-ProLabo. Lithium chloride (LiCl) was purchased from Merck. All salts were 99% pure. MilliQ water (≥18.2 MΩ·cm) used throughout the synthesis was obtained by a Millipore MilliQ® biocel, which used a Q-grade® column.

Synthesis of the extractant

[N_{8888}][monensin] was obtained by adding tetraoctylammonium chloride (1.17 g, 2.33 mmol) dissolved in 50 mL toluene to an aqueous solution of an equimolar amount of monensin salt (1.61 g, 2.33 mmol, 50 mL) and stirred for 3 h at room temperature. The organic phase was washed with water in order to remove the remaining chloride (6 times with 50 mL demineralised water). Chloride content was checked to be negligibly low by adding $AgNO_3$ to the last water phase and observing no AgCl precipitate. Afterwards, toluene was removed under reduced pressure using a rotary evaporator (BUCHI Rotavapor® R-3) at 50 °C. The product was obtained in the form of a white solid (2.936 g). Yield: 92% MS (ESI): Calculated for $[N_{8888}(C_{32}H_{68}N)]^+$ m/z: 467.0; found m/z: 466.7 and calculated for $[\text{Monensin}(C_{36}H_{61}O_{11})]^-$ m/z: 669.9; found m/z: 669.4. Elemental analysis: found (%): C, 73.0; H, 11.6; N, 1.41; calc. for $C_{68}H_{129}O_{11}N$: C, 71.85; H, 11.44; N, 1.23; O, 15.48. T_m >378 K, two degradation points were observed T_d = 463 K and 552 K.

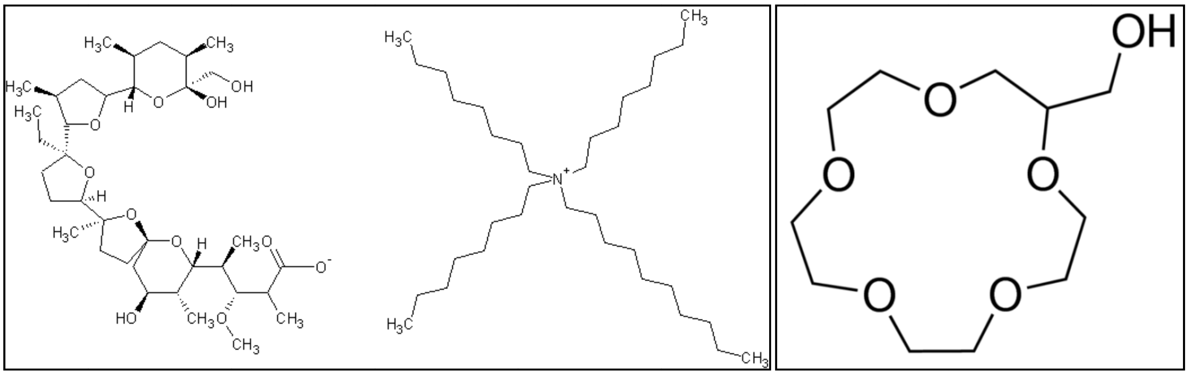

Figure 9.1. *On the left, the extractant tetraoctylammonium monensin, [N$_{8888}$][monensin], that was developed during this research and on the right the structure of 2-hydroxymethyl-15-crown-5.*

Characterization of the IL

The purity of the IL was determined using ^{1}H NMR on a 400 MHz Bruker nuclear magnetic resonance (NMR) spectrometer. The decomposition temperature was determined with a thermo-gravimetric analysis (TGA) Q 500 apparatus (TA instruments, USA) at a scan rate of 10 $K\cdot min^{-1}$ under a nitrogen flow. The spectra were analysed with TG instruments software. Differential scanning calorimetry (DSC) Q 1000, and Perkin Elmer Pyris 1 were used to obtain the melting temperature with a scan rate of 10 °C min^{-1}. Electrospray-ionisation combined with mass spectrometry (ESI-MS) was used to analyse the IL after synthesis with acetonitrile as eluens. An Agilent Technologies 1200 series ESI-MS was used with acetonitrile:water 90:10 v/v as eluens working with an Agilent mass hunter workstation data acquisition.

Salt extraction and regeneration procedure

Two metal salt solutions were used to test the extraction efficiency of [N$_{8888}$][monensin]. One solution contained 1 g/L of KCl, NaCl and LiCl and the other contained 1 $g\cdot L^{-1}$ of Li and 2 $g\cdot L^{-1}$ of Na, K, Mg and Ca from their chloride salts. At the beginning, 0.5 g of [N$_{8888}$][monensin] was dissolved in 10 mL of toluene. For the first salt solution, 5 mL of the toluene solution was mixed with 5 mL salt solution and for the second salt solution only 1 mL of the toluene solution and 1 mL of the salts solution was applied. Extraction of the first salt solution was also repeated for an equimolar amount of sodium monensin or 2-hydroxymethyl-15-crown-5 dissolved in toluene. For the regeneration, samples of 1 mL of the 5 mL toluene solution that was applied for the extraction of the first salt solution were afterwards mixed with 1 mL of a 0.1 M HCl solution or a 0.1 M acetic acid solution or MilliQ water. The samples were each time stirred for 2 h on a vortex mixer (Heidolph multireax) and then placed in a centrifuge (Allegra TM X-12R, Beckman coulter) for 5 min at 3750 rpm.

Analysis of the water phase after extraction

Concentrations of the cations present in the water phase were measured with a Perkin Elmer, precisely Induced Coupled Plasma (ICP), which used an optical emission spectrometer Optima 5300DV. Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-AES has a detection limit of 25-250 $\mu g{\cdot}L^{-1}$, with an uncertainty of 1.4-2%.

Extraction efficiency (*E%*) is calculated by:

$$E(\%) = \left\{\frac{(c_0 - c_1)}{c_0}\right\} \times 100 \tag{1}$$

where c_0 and c_1 are the total metal concentration ($mg{\cdot}L^{-1}$) in the aqueous phase before and after metal extraction, respectively. Furthermore, the molar ratio x_i of salt extracted over the amount of extractant applied was calculated via:

$$x_i = \frac{n_i}{n_{ex}} \tag{2}$$

in which n_i stands for the molar amount of salt extracted and n_{ex} is the molar amount of extractant being applied.

Regeneration (*R%*) is calculated by:

$$R(\%) = \left\{\frac{c_2}{c_3}\right\} \times 100 \tag{3}$$

where c_2 stands for the metal concentration ($mg{\cdot}L^{-1}$) observed in the aqueous phase after regeneration and c_3 is the metal concentration ($mg{\cdot}L^{-1}$) in the organic phase and is determined by $c_0 - c_1$.

The molar concentration of the salt removed was calculated from the difference of the total cation concentrations in the aqueous phase before and after the extraction.

Solubility experiment

The solubilities of [N_{8888}][oleate] and sodium monensin ([Na][monensin]) was tested by adding of each compound 1g to a test tube containing 27.5 mL of the metal salt solution consisting out of 1 $g{\cdot}L^{-1}$ of KCl, NaCl and LiCl. Both samples were then shaken for 48 h at 25 °C on a multi vortex with a speed of 2000 rpm. Afterwards the samples were filtered over a Whatman filter paper (cat. No. 1005110) and analyzed for its total organic carbon content

(TOC). TOC c was determined on a Shimadzu TOC-LCPH with a detection limit of 1.00 $mg{\cdot}L^{-1}$.

9.3. Results and discussion

A white solid powder was obtained after the straightforward synthesis of the extractant, [N_{8888}][monensin]. Determination of the melting point showed that the melting point was above 100°C. Therefore, this compound cannot be called an IL and can better be referred to as a solid organic crystal or an organic ionic crystal.

Table 9.1. *Extraction efficiencies (E%) for [N_{8888}][monensin] dissolved in toluene (A) of a salt (Li, Na, K) solution as well as to the extraction efficiencies of [Na][monensin] (B) and 2-hydroxymethyl-15-crown-5 (C).*

	E_A (%)	x_{iA}	E_B (%)	x_{iB}	E_c (%)	x_{iC}
K	10	0.062	2.8	0.0093	2.3	0.000013
Na	51	0.54	-4.1	-0.020	2.6	0.000029
Li	9.4	0.29	1.1	0.0049	3.2	0.00047

Afterwards, first tests were performed to see if the organic ionic crystal shows Na extraction, see Table 9.1. It was observed that the extractant showed a distinct selectivity towards Na compared to Li and K. The extraction results for [N_{8888}][monensin] were also compared with the selective removal of Na by the precursor, sodium monensin ([Na][monensin]) (Table 9.1). First of all, it was visually noticed that it was not possible to dissolve [Na][monensin] in toluene, but by applying sonification it was possible to suspend it homogeneously. Next to this, no extraction of Na was observed. Instead, negative extraction efficiencies were observed. This is most likely due to some exchange of the Na in the [Na][monensin] by K or Li. The extraction with 2-hydroxymethyl-15-crown-5, which is generally accepted to be known as a good sodium selective crown ether extractant,[39] did not show a significant extraction and certainly no selectivity for the same alkali salt solution with the same applied conditions. This indicates once more how remarkable it is to observe such a fast and high selective extraction for sodium by the [N_{8888}][monensin] organic ionic crystal.

Table 9.2. *Extraction efficiencies for a test solution containing the metals Li, Na, K, Mg and Ca using [N_{8888}][monensin].*

	Li	Na	K	Mg	Ca
E(%)	1.0	41	2.1	1.5	1.2
x_i	0.028	0.80	0.023	0.026	0.014

Checking the extraction efficiency of the organic ionic crystal [N_{8888}][monensin] for a test solution containing the most common metal cations in drinking and irrigation water confirms again the very high selectivity for Na (Table 9.2). In this case, the Na removal corresponded to a ratio of 0.80 mol Na per mol of extractant. Comparing these results to membranes containing monensin reported in literature shows again that this organic ionic crystal has a remarkable high selective absorption for Na.[36]

Table 9.3. *Regeneration efficiencies (R) for solution of [N_{8888}][monensin] dissolved in toluene after the extraction of alkali metals presented in Table 9.1 (E_A) and there extraction efficiencies (E) afterwards towards the same alkali solution applied for Table 9.1.*

	R_{HCl} (%)	$R_{acetic\ acid}$ (%)	R_{H2O} (%)	E_{HCl} (%)	$E_{acetic\ acid}$ (%)	E_{H2O} (%)
K	32.1%	30.4%	28.8%	8.5%	8.8%	11.2%
Na	100.0%	100.0%	56.0%	6.6%	8.8%	38.5%
Li	9.8%	9.4%	9.3%	9.0%	9.3%	9.6%

Regeneration and reuse of the extractant was investigated with 0.1 M HCl, 0.1 M acetic acid and MilliQ water in a next experiment (Table 9.3). Tests were performed on the toluene solution containing [N_{8888}][monensin] that was applied for extraction of an aqueous solution of 1 g/L of LiCl, KCl and NaCl presented in Table 9.1. Results show that regeneration can efficiently be done by applying an acid (i.e. acetic acid or HCl). However, the extractant losses its selective extraction capability. It is assumed that the higher regeneration with acids is caused by the protonation of monensin together with the formation of a very water soluble sodium salt. Reuse of the organic ionic crystal after acidic regeneration is not possible and indicates that the organic ionic crystal should first be deprotonated before reuse or that the monensin ion is not stable towards acids. Regeneration is to a lesser extent also possible with MilliQ water, from which afterwards still some sodium selectivity is observed. Although the extraction and regeneration results look very promising, further experiments are necessary to investigate why the organic ionic crystals cannot be reused. This would indicate if alternative regeneration procedures have to be applied or if more stable monensin based complexes have to be developed that still show a high sodium selectivity. Understanding and overcoming this problem will then result in a high selective organic ionic crystal that can be implemented in ion-exchange resins or membranes.

Next to the extraction efficiencies, also the suspension of [Na][monensin] in water was compared to that of [N_{8888}][monensin] in water. When shaking the two compounds with the salt (Li, Na and K) solution, it was already noticed that [Na][monesin] formed a white emulsion with the water phase, while [N_{8888}][monensin] does not form an emulsion and prefers to stick to the inner wall of the test tubes. Analysis of the water phase showed that [Na][monensin] has a solubility in water of 72 $mg \cdot L^{-1}$, while [N_{8888}][monensin] has a solubility in water of only 44 $mg \cdot L^{-1}$. From this result, it can be concluded that replacing the sodium ion by the [N_{8888}] cation in the monensin salt results in an almost twofold reduction of the solubility in water, thereby preventing the loss of this valuable organic ionic crystal.

9.4. Conclusions

Results showed that the organic ionic crystal, [N_{8888}][monensin] is an ideal extraction agent for selective Na removal (41%) from a mixed salt solution containing LiCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$. Comparing the sodium selectivity and extraction kinetics with a known sodium extractant 2-hydroxymethyl-15-crown-5 stresses the high selectivity of this novel organic ionic crystal. Furthermore, changing the Na cation for [N_{8888}] to obtain the organic ionic crystal [N_{8888}][monensin] resulted in a lower solubility of this organic ionic crystal in the aqueous phase. Full regeneration of this organic ionic crystal is possible by applying acidic solutions (0.1 M HCl or 0.1 M acetic acid). However, this regeneration step limits its reuse.

9.5. References

1 R. W. Tuthill and E. J. Calabrese, *Arch. Environ. Heal. An Int. J.*, 2013, **34**, 197–203.

2 L. A. Sapirstein, W. L. Brandt and D. R. Drury, *Exp. Biol. Med.*, 1950, **73**, 82–85.

3 E. J. Calabrese and R. W. Tuthill, *Arch. Environ. Heal. An Int. J.*, 1977, **32**, 200–202.

4 L. Prior, A. Grieve and B. Cullis, *Aust. J. Agric. Res.*, 1992, **43**, 1067.

5 R. H. Nieman, *Bot. Gaz.*, 1962, **123**, 279–285.

6 J. Han, J. W. Carey and J. Zhang, *J. Appl. Electrochem.*, 2011, **41**, 741–749.

7 S. Biswas, V. H. Rupawate, S. B. Roy and M. Sahu, *J. Radioanal. Nucl. Chem.*, 2014, **300**, 853–858.

8 B. Onghena, J. Jacobs, L. Van Meervelt and K. Binnemans, *Dalt. Trans.*, 2014, **43**, 11566.

9 N. V Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.

10 J. F. Brennecke and E. J. Maginn, *AIChE J.*, 2001, **47**, 2384–2389.

11 W. Wang, H. Yang, H. Cui, D. Zhang, Y. Liu and J. Chen, *Ind. Eng. Chem. Res.*, 2011, **50**, 7534–7541.

12 M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391–1398.

13 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.

14 L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler and S. Hann, *Water Res.*, 2011, **45**, 4601–4614.

15 T. Vander Hoogerstraete, S. Wellens, K. Verachtert and K. Binnemans, *Green Chem.*, 2013, **15**, 919–927.

16 S. Wellens, R. Goovaerts, C. Moeller, J. Luyten, B. Thijs and K. Binnemans, *Green Chem.*, 2013, **15**, 3160–3164.

17 S. Wellens, B. Thijs and K. Binnemans, *Green Chem.*, 2012, **14**, 1657–1665.

18 X. Sun, Y. Ji, F. Hu, B. He, J. Chen and D. Li, *Talanta*, 2010, **81**, 1877–83.

19 T. Vander Hoogerstraete, B. Onghena and K. Binnemans, *J. Phys. Chem. Lett.*, 2013, **4**, 1659–1663.

20 D. Kogelnig, A. Stojanovic, F. Jirsa, W. Körner, R. Krachler and B. K. Keppler, *Sep. Purif. Technol.*, 2010, **72**, 56–60.

21 S. Chun, S. V. Dzyuba and R. A. Bartsch, *Anal. Chem.*, 2001, **73**, 3737–3741.

22 M. L. Dietz, J. A. Dzielawa, I. Laszak, B. A. Young and M. P. Jensen, *Green Chem.*, 2003, **5**, 682.

23 V. Cocalia, J. Holbrey, K. Gutowski, N. Bridges and R. Rogers, *Tsinghua Sci. Technol.*, 2006, **11**, 188–193.

24 S. Dai, Y. H. Ju and C. E. Barnes, *J. Chem. Soc. Dalt. Trans.*, 1999, 1201–1202.

25 A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin and R. D. Rogers, *Ind. Eng. Chem. Res.*, 2000, **39**, 3596–3604.

26 H. Luo, S. Dai, P. V Bonnesen, A. C. Buchanan, J. D. Holbrey, N. J. Bridges and R. D. Rogers, *Anal. Chem.*, 2004, **76**, 3078–3083.

27 H. Luo, S. Dai and P. V Bonnesen, *Anal. Chem.*, 2004, **76**, 2773–2779.

28 M. L. Dietz and J. a Dzielawa, *Chem. Commun. (Camb).*, 2001, 2124–2125.

29 D. Parmentier, S. J. Metz and M. C. Kroon, *Green Chem.*, 2012.

30 V. M. Egorov, D. I. Djigailo, D. S. Momotenko, D. V. Chernyshov, I. I. Torocheshnikova, S. V. Smirnova and I. V. Pletnev, *Talanta*, 2010, **80**, 1177–1182.

31 J. R. Harjani, T. Friščić, L. R. MacGillivray and R. D. Singer, *Dalt. Trans.*, 2008, 4595.

32 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.

33 A. E. Visser, R. P. Swatloski, W. M. Reichert, J. H. Davis Jr., R. D. Rogers, R. Mayton, S. Sheff and A. Wierzbicki, *Chem. Commun.*, 2001, 135–136.

34 H. Luo, S. Dai, P. V. Bonnesen and A. C. Buchanan, *J. Alloys Compd.*, 2006, **418**, 195–199.

35 S. Tang, G. A. Baker and H. Zhao, *Chem. Soc. Rev.*, 2012, **41**, 4030–4066.

36 E. M. Choy, D. F. Evans and E. L. Cussler, *J. Am. Chem. Soc.*, 1974, **96**, 7085–7090.

37 K. Tohda, K. Suzuki, N. Kosuge, H. Nagashima, K. Watanabe, H. Inoue and T. Shirai, *Anal. Sci.*, 1990, **6**, 227–232.

38 S. J. Pace and C. Wang, 1996.

39 Y. Takeda, K. Katsuta, Y. Inoue and T. Hakushi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 627–632.

Chapter 10

Techno-economical evaluation of metal extraction with ionic liquids

10.1. Technical feasibility

In chapter 6, a proof-of-concept for the technically feasible of a continuous setup for selective metal extraction based on ILs has been presented. **The requirements for an IL** to be applied in a continuous setup for metal extraction are:

- The IL has to be very **hydrophobic** in order to minimize losses of the valuable IL and to prevent the pollution of the treated water phase with organic ions from the IL.
- The IL needs to be **able to extract metals** and the extraction mechanism should be based on **ion-pair extraction** and definitely not based on ion-exchange. If the extraction would be based on ion-exchange then an increasing metal ion extraction will be accompanied by increasing solubilisation of the IL in the aqueous phase, which cannot be regarded as sustainable. A group of ILs that are an exception to this rule are tetraalkylammonium or tetraalkylphosphonium chloride or bromide ILs that are able to extract 3d transition metal ions as tetrachloro or tetraboro complexes.[1,2]
- The ILs should be **selective towards the metal or group of metals** that one wants to remove keeping also in mind the physical parameters of this stream, i.e. pH, chloride concentration, total salt concentration, dissolved organic compounds, etc. The choice of IL depends on the metal interacting functional groups that the IL is bearing and on it extraction mechanism.
- The **viscosity** of the IL should be **low**, i.e. comparable with conventional organic solvents, because this lowers the cost for pumping the liquid and, more importantly, it speeds up the extraction kinetics of the liquid. Nowadays, when viscous ILs are applied for metal extraction, one has to heat up the IL and metal solution of interest to elevated temperatures (>40-60°C), resulting in a huge energy demand to perform these extractions in a continuous mode. Another option is to dilute the highly viscous IL with an organic solvent, which is an additional cost and has extra consequences related to the pollution of the air and the water phase and its toxicity. The viscosity of an IL depends mainly on its structure and on the water uptake.[3]
- It should be **possible to regenerate** the IL in a cost-effective way in which the extracted metals are obtained as a valuable product without preventing the reuse of the IL.
- Although the IL can be reused after metal extraction, one should preferably select an IL that is **not too expensive** or an IL that can be easily synthesized from cheap starting materials to be able to economically compete with existing desalination techniques.
- Working with water also includes that the IL should be **non-toxic** and easily

biodegradable, hereby minimizing the post treatment step after treating the water, only in specific industrial cases this factor is of a less importance. Still, in concern to its biodegradability, the IL should be stable during operation.

These requirements were checked for the fatty acid based IL [P_{8888}][oleate] that was developed during this research. All requirements except one are met:

[P_{8888}][oleate] has a very low water solubility; after mixing the IL with a 0.05 M NaCl only 31.5 ppm of organics were detected in the water phase. Indicating that this IL is even more hydrophobic then common hydrophobic hexafluorophosphate and bistriflimate ILs.[4,5]

[P_{8888}][oleate] can selectively extract metals depending on the pH and chloride concentration and its mechanism of metal extraction is based on ion-pair extraction.

[P_{8888}][oleate] also has a very low viscosity for an IL due to the high water uptake which accelerates the extraction kinetics and accelerates the phase disengagement after mixing.

Regeneration can be done by applying cheap and safe sodium oxalate as a stripping solution. The IL can directly be reused and the extracted metals are recovered as oxalate complexes, which can undergo calcination into the pure metal oxides.

[P_{8888}][oleate] is synthesized via a simple method based on the precursors oleic acid and tetraoctylphosphonium bromide. Oleic acid is a cheap, biodegradable compound. The price of the IL on a commercial scale is estimated to be around €33.7 /L, which is an average price for an IL, but still more expensive than conventional solvents (on average €1 /L).[6]

The only requirement that is not fulfilled is the low toxicity of the IL, even though the IL was developed with the biodegradable oleic acid as anion. However, to make sure that the IL was very hydrophobic and did not emulsify, it was necessary to apply a bulky hydrophobic cation, such as tetraoctylphosphonium. It is known that this cation disrupts cell membranes due to its high hydrophobic or liphophilic character. Concluding that although the risk of polluting the treated water phase is minimized, the traces of the IL dissolved into the water phase are more toxic towards cellular organisms.

All bulky hydrophobic ammonium or phosphonium cations will bear this toxicity due to their lipophilicity, but a way to reduce their toxicity is by introducing ether or amide functionalities into their structure. Unfortunately, this will also have an effect on the water solubility, viscosity, density and stability of the IL. Future developments and selection of the cation will have to be done carefully, so that the properties of the resulting ionic liquids meet all conditions. A good alternative cation could be the ester derivative of cocamidopropyl betaine, which is applied as a safe hydrophobic tetraalkylammonium compound in bath products and cosmetics.

10.2. Economical feasibility

Also in chapter 6 an economical analysis was performed to compare the continuous metal extraction setup based on ionic liquids with conventional ion-exchange resins. This analysis indicates that metal removal with ion-exchange resins is cheaper in construction, but also cheaper in maintenance due to the very stable ion-exchange resins, the very low energy consumption and the easiness of regeneration using a brine solution. This is also the reason why ion-exchange resins are a very reliable and robust technique for water softening or selective metal removal up to now. Thus, IL based metal extraction systems are economically outcompeted by ion-exchange resins. However, the products of ion-exchange are pure water and a concentrated brine. No valuable metals are recovered with this conventional technique. If brine disposal is an issue or if the production of a very pure metal stream is the main product instead of obtaining pure water, then the IL based metal extraction system can be a good alternative, especially because the metal can be a valuable side product, significantly improving the business case. Moreover, if further research points out that ILs can also recover very valuable or toxic non-ionic metal complexes, which ion-exchange resin cannot extract, in a continuous mode, then the IL system will also become a valuable selective metal extraction technique. Examples of such non-ionic metal complexes that cannot be recovered using ion-exchange resins are metal catalysts, such as the Wilkinson's catalyst (chlorotris(triphenylphosphine)rhodium(I)) that is used for the hydrogenation of alkenes[7] or medicinal metal complexes, such as cisplatin to defeat tumors[8] or gadolinium complexes to target tumors[9] in hospital water. Also the removal of metal nanoparticles from waste water can result in a strong business case.[10]

10.3. Comparison with other desalination techniques that apply ILs

10.3.1. The AquaOmnes process

AquaOmnes is a new technology based on fluorinated ILs that removes salts from water through saline water deionisation by liquid-liquid absorption launched by the company Adionics.[11] They claimed that their technology has three main benefits:

-its energy consumption is very low,

-it has a low liquid discharge,

-it is a low cost effective technology.

In 2015 it was reported that Adionics adapted its AquaOmnes desalination technology to be fitted into existing desalination plants and into the oil and gas industry, but so far a commercial application has not been found.[12] The new variant of AquaOmnes proposes a solution designed to desalinate brines from existing plants, which is robust, more cost-effective, more compact, that works at ambient pressure and that makes it possible to highly concentrate the waste. Furthermore, they state that their technology reduces a plant's costs by nearly 30% in terms of CAPEX and at least 50% in terms of OPEX, compared to the best-of-breed desalination processes.[12]

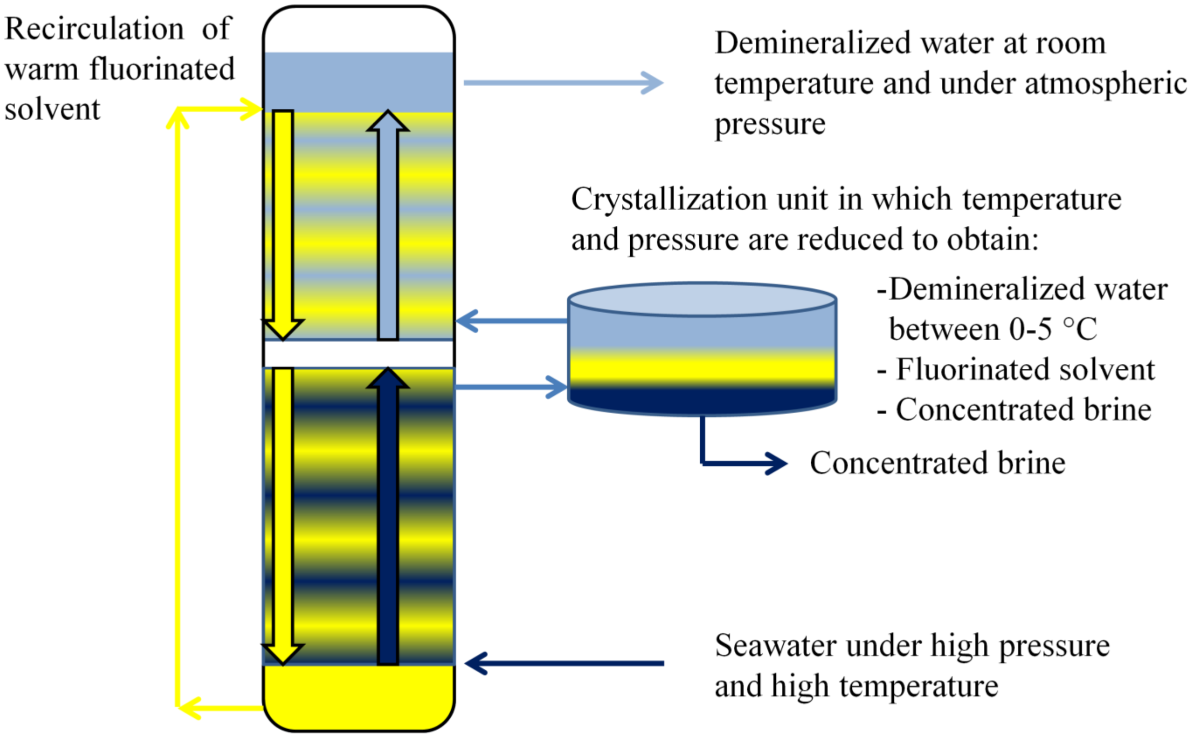

Figure 10.1. *Overview of the AquaOmnes process that is based on fluorinated ILs or fluorinated non-ionic surfactants as salt extractants dissolved in a fluorinated solvent which acts as a heat exchanger.*

The patent of Adionics showed that their technology is based on fluorinated ILs or fluorinated non-ionic surfactants as salt extractants dissolved in a fluorinated solvent which acts as a heat exchanger.[13] The solubility of fluorinated compounds in water is very low (≤10 ppm). On the contrary, fluorinated compounds are very persistent and toxic to aquatic environments so they should be removed from the treated water at all cases. Moreover, the use of an additional fluorinated solvents is necessary, because the mechanism of metal extraction for the fluorinated ILs is based on ion-exchange and without the fluorinated solvent the fluorinated organics of the IL would leach to the water phase. In the patent, the regeneration of the fluorinated IL is done by cooling down the metal loaded IL to obtain a high concentrated brine solution, see Figure 10.1. This is a very simple process for regeneration. Biggest disadvantage of the process is the high operation temperature (≥60 °C) in order to get good and fast kinetics for the ion-exchange process combined with cooling, resulting in a very high energy cost, especially if one takes into account that an average desalination plant treats 4700 m³ water per day.[14]

Comparison of the pro and cons from the AquaOmnes process with the fatty acid based continuous metal extraction setup that is develop in this research:

The AquaOmnes process extracts all different salts simultaneously from a saline solution, except for sodium and chloride, while with the fatty acid based IL only specific metals are extracted depending on the pH and chloride concentration. The IL process described in this thesis is thus much more selective.

The losses of fluorinated compounds towards the water phase are extremely low; however these fluorinated compounds are very persistent and toxic towards aquatic life. In comparison, the fatty acid based IL is somewhat more soluble (5 ppm), but much more biodegradable and less toxic.

The loss of fluorinated organic ions of the IL due to the ion-exchange mechanism is overcome by applying a fluorinated solvent in the AquaOmnes process. Due to this, regeneration can be done by applying a concentrated sodium chloride solution resulting in the formation of a very concentrated brine stream. Contrary, in this work the extraction mechanism was not based on ion-exchange, but on ion-pair extraction and the regeneration of the IL was done by applying sodium oxalate as stripping solution. Sodium oxalate is more expensive compared to sodium chloride, but due to the selectivity of the fatty acid based IL a more valuable product is obtained.

During the regeneration a brine waste stream is produced, while in the continuous metal extraction process with the fatty acid based system a valuable metal stream is obtained.

The main disadvantage of the AquaOmnes process is that it has to be operated at elevated temperatures (≥60 °C) due to the extraction kinetics, which results in a significant energy cost, while the IL process developed in this research can be operated at room temperature with high extraction efficiencies due to its low viscosity.

10.3.2. Ionic liquids implemented in forward osmosis

Recently, a new paper about desalination using ILs appeared. The authors used the IL as new draw solutes for forward osmosis (FO) desalination.[15] FO is the transport of water from a salt solution towards an electrolyte solution with a higher osmotic pressure (in this case IL + water) through a semi-permeable membrane. The result is a more concentrated brine solution and a diluted electrolyte stream. FO is only feasible if the electrolyte can be easily separated from the water in order to obtain pure water and the original electrolyte (= draw solute). Cai *et al.* reported the use of hydrophobic ILs, which are completely composed out of ions, with a lower critical solubility temperature (LCST) as ideal draw solutions (see Figure 10.2).[15] Due to the LCST these ILs are soluble in water until a certain temperature is reached and then the IL phase and the water phase separate. Such a temperature controllable draw solute is very attractive because of its simple water separation mechanism and the absence of using additional chemicals. Afterwards the water phase that is obtained after heat separation undergoes nanfiltration (NF, this process is identical to RO but utilized membranes with bigger pore sizes and hereby needs less pressure and energy) to remove dissolved IL. Due to the less energy consumption of NF compared to RO, the authors state that this process is very (electrical) energy-efficient, when a minimum amount of thermal energy can be delivered from low grade industrial waste heat or solar thermal energy. Yet, in chapter 8 when the $[P_{8888}]$[oleate] IL was tested as concentrated phase in electrodialysis, it was noticed that the IL that we applied although it also has a big osmolality, had only a very low osmotic flux (0.017 $l/m^2 \cdot h$) or water transport in time through the membrane. Data in the article of Cai *et al.* learns us that this flux for the IL, tetrabutylphosphonium 2,4-dimethylbenzenesulfonate $[P_{4444}]$[DMBS], that is applied in this research, is still low (70 wt% draw solution can generate a water flux of 1.5 $l/m^2 \cdot h$ against a feed of 1.2 M NaCl at 14 ± 1 °C), although this IL has a high osmalality (30 wt% solutions has a osmolality of 1.34 osmol kg^{-1}). Seawater (contains on average 0.599M NaCl) RO operates with water fluxes between 12-15 $l/m^2 \cdot h$.[16] Furthermore, if this process will be utilized for drinking water purposes, then the authors should be able to guarantee that no IL will leak to the water phase, because they have a similar toxic effect on cell membranes as the ILs applied in this work.

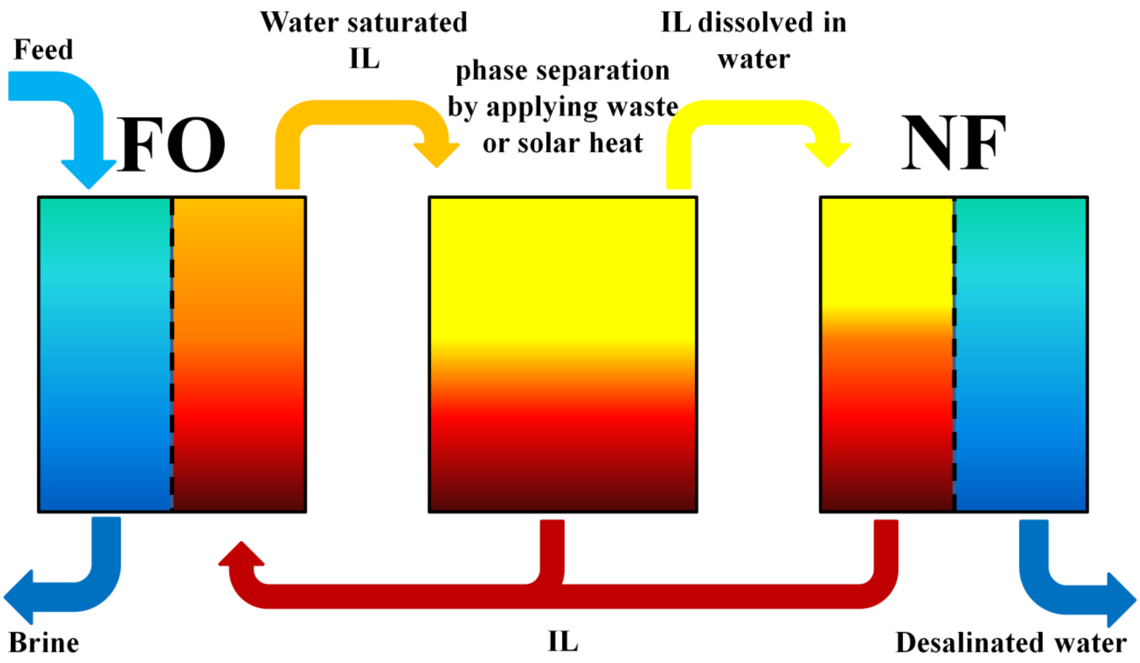

Figure 10.2. *Overview forward osmosis desalination with ionic liquids as draw solution in which the desalinated water is obtained by nanofiltration.*

10.4. References

1. D. Kogelniga, A. Stojanovic, F. Jirsaa, W. Körner, R. Krachler, B. K. Keppler, Sep. Purif. Technol. 72, 56–60 (2010).
2. M. Regel-Rosocka, Sep. Purif. Technol. 66, 19–24 (2009).
3. D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans, M. C. Kroon, Ind. Eng. Chem. Res. 54, 5149–5158 (2015).
4. C. M. S. S. Neves, M. L. S. Batista, A. F. M. Cláudio, L. M. N. B. F. Santos, I. M. Marrucho, M. G. Freire, J. A. P. Coutinho , J. Chem. Eng. Data 55, 5065–5073 (2010).
5. M. G. Freire, P. J. Carvalho, R. L. Gardas, I. M. Marrucho, L. M. N. B. F. Santos, J. A. P. Coutinho, J. Phys. Chem. B 112, 1604–1610 (2008).
6. N. V. Plechkova and K. R. Seddon, Chem. Soc. Rev. 37, 123–150 (2008).
7. D. J. Cole-Hamilton, Science 299, 1702–6 (2003).
8. L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, R. Krachler, B. K. Keppler, S. Hann, *Water Res.* **45,** 4601–4614 (2011).
9. R. Torkaman, M. A. Moosavian, J. Safdari, M. Torab-Mostaedi, *Ann. Nucl. Energy* **62,** 284–290 (2013).
10. J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, *J. Am. Chem. Soc.* **124,** 4228–4229 (2002).
11. Adionics unveils new desalination technology - Water Technology. *www.water-technology.net* (2014). at <http://www.water-technology.net/news/news-adionics-unveils-new-desalination-technology-4262151>
12. Adionics adapts its AquaOmnes disruptive desalination technology to existing desalination plants and to the oil and gas industry. *AMEInfo.com* (2015). at <http://ameinfo.com/energy/oil-and-gas/extraction/adionics-adapts-aquaomnes-disruptive-desalination-technology-existing-desalination-plants-oil-gas-industry/>
13. G. De Souza, Unite de pretraitement d’eau au moyen d'un liquide fluore. (2011). at <http://www.google.com/patents/EP2391584A1?cl=fr>
14. Desalination by the Numbers. *interantional desalination association* (2015). at <http://idadesal.org/desalination-101/desalination-by-the-numbers/>
15. Y. Cai, W. Shen, J. Wei, T. H. Chong, R. Wang, W. B. Krantz, A. G. Fane and X. Hu, *Environ. Sci. Water Res. Technol.* **1,** 341–347 (2015).
16. L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot, P. Moulin, *Water Res.* **43,** 2317–48 (2009).

Chapter 11

Conclusion and outlook

11.1. Conclusion

A continuous metal extraction setup based on ionic liquids (ILs) is a promising novel technique for selective metal removal and valorisation of the extracted metals. For this purpose, the fatty acid based IL tetraoctylphosphonium oleate ([P_{8888}][oleate]) was applied. This IL was synthesized via a simple method based on the precursor tetraoctylphosphonium bromide and the cheap and biodegradable oleic acid (estimated commercial ton scale price: €30 /kg IL). This fatty acid based IL has a very low water solubility and its metal extraction mechanism is based on ion-pair extraction, so that losses of this valuable IL towards the aqueous phase are minimized.

A more thorough investigation on its extraction mechanism proved that the metals Co(II) and Ni(II) were extracted in the pH range (6-8) by the formation of metal carboxylate tetraalkylammonium complexes, whereas Zn(II) gets extracted as a metal chloride carboxylate tetraalkylammonium complex. So, different metal extraction mechanisms occur depending on the ability of the extracted metals to form chloro-complexes. It was concluded that the metal extraction efficiency of the IL strongly depends on pH and chloride concentration. Very good extraction efficiencies and selectivities are observed for transition metals ($MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$) and rare earth metals ($LaCl_3$, $NdCl_3$, $SmCl_3$, $DyCl_3$, $ErCl_3$ and $YbCl_3$) at a pH ranging from 6-8 compared to alkali (LiCl, NaCl and KCl) and alkaline earth metals ($MgCl_2$ and $CaCl_2$). Also, a gap of one pH unit is observed for the optimal extraction of rare earth metals and the transition metals, making this IL suitable for the separation of these metals from each other at different pH values.

Unfortunately, direct electrodeposition, which would be very sustainable because no additional chemicals would have to be added to the system, is not feasible for regeneration of the fatty acid based IL. Applying acids or bases for the regeneration is also not possible due to the protonation of the oleate anion (in the case of acids), which prevents further metal extraction, or due to the formation of an amphiphilic molecule (sodium oleate in the case of bases (sodium hydroxide in this case)), which prevents phase separation of the IL phase and water phase. Regeneration of the IL can partially be done by applying a cheap and safe sodium oxalate solution as a stripping agent. In this way, the extracted metals are recovered as oxalate complexes, without preventing direct reuse of the IL for metal extraction. The only major disadvantage of the fatty acid based IL is that due to its hydrophobic character it is also very liphophilic and therefore very disruptive towards cell membranes.

Good and stable extraction efficiencies were obtained for the continuous metal extraction setup based on [P_{8888}][oleate]. Excellent selective extraction of cobalt was observed starting from a mixed (Ca/Co/K) metal solution. In the work reported in this thesis, a concentrated cobalt stream was obtained containing 543 $mg{\cdot}L^{-1}$ of Co, 56 $mg{\cdot}L^{-1}$ of Ca and no detectable K, when working with a feed stream containing 1.0 $g{\cdot}L^{-1}$ of the metals Ca/Co/K being treated at a flow rate of 20 $mL{\cdot}min^{-1}$. It was very positive to notice that the extraction efficiency of cobalt was stable over time, indicating that the extraction and stripping in the setup reach a stable stationary state. No degradation of the IL was observed that prevents further metal extraction. Experiments also showed that lower flow rates (15 $mL{\cdot}min^{-1}$) resulted in higher extraction (>95%) and regeneration values (>70%). Economic analysis demonstrates that the IL based process that was developed was both more expensive in investment cost (CAPEX) and operational cost (OPEX) compared to a process based on ion-exchange resins, especially in case demineralised water is the only product. However, if the recovery of valuable metals is also taken into account and/or in case brine disposal is an issue, then continuous IL based metal extraction systems are a promising alternative.

In this PhD work, it was also investigated if simultaneously electrospraying of a metal solution with an IL could result in improved metal extraction compared to physical mixing. A stable spray (cone-jet mode) was obtained with a coaxial nozzle at a potential of 5 kV when the IL is the outer liquid with a flow rate of 1.2 $mL{\cdot}h^{-1}$ and the aqueous phase is the inner liquid with a flow rate of 1 $mL{\cdot}h^{-1}$. The metal extraction efficiencies of the IL during conventional physical mixing were already very high for transition metals (E_{Co} 98% and E_{Mn} 98%) and no improvement in metal extraction was observed by applying electrospray (E_{Co} 83% and E_{Mn} 80%). Nevertheless, higher separation factors were observed for the valuable transition metals compared to the light metals due to electrospraying. For example, the separation factor of Co over Ca was 5.0when electrospraying was applied at 5 kV compared to 3.7 with physical mixing.

The combination of hydrophobic metal selective ILs with electrodialysis (ED) resulted in a process that can both selectively desalinate water and concentrate specific transition metals ions. The proof of concept was given that an ED process can be operated with a hydrophobic metal selective IL as concentrate phase. Removal ratio of ions out of the diluate phase is still depending on the ED process and the uptake of ions in the concentrate phase depends on the selectivity of the IL. Combining ILs as concentrate phase into the ED stack resulted in minimized water transport, so that leakage of the IL towards the water phase was prevented.

Finally, it was tried to develop a completely novel sodium selective ionic liquid on basis of the natural ionophore sodium monensin. As a result, a solid organic ionic crystal

([N_{8888}][monensin]) was obtained, which showed a remarkably high selective Na extraction (41%) from a mixed salt solution containing LiCl, NaCl, KCl, $MgCl_2$ and $CaCl_2$. The solubility of the monensin salt in water decreased by replacing the sodium cation by the [N_{8888}] cation. It also turned out that this organic ionic crystal was not liquid at room temperate, which prevented the use of this organic ionic crystal for liquid-liquid extraction in a continuous metal extraction setup without additional solvent. Nevertheless, this organic ionic crystal opens the possibility to be implemented in membranes and/or ion-exchange resins. Complete regeneration of the ionophore was possible by applying acidic solutions (0.1 M HCl or 0.1 M acetic acid). However, this regeneration step limits its reuse.

The initiative to start my PhD project with ILs was based on the fact that it should be more energetically effective to desalinate water if one can selectively remove the salt from the seawater, see chapter 1. Nevertheless, from chapter 6 one can observe that each type of metal gets extracted at a different pH and chloride concentration with the fatty acid based IL. And that extraction of monovalent ions (Na and K) leads to the formation of the emulsifier, sodium oleate, that is disruptive for the phase separation. Meaning that full desalination of (sea)water with the develop fatty acid based IL is not possible. It is also assumed by the author, due to the knowledge gained throughout this PhD project that full desalination of seawater with ILs will not be feasible.

11.2. Outlook

Still many questions have to be answered before a continuous metal extraction setup based on fatty acid based ILs can be implemented on an industrial scale. Next step in the research is to operate the continuous metal extraction setup based on ILs for a longer period of time (>8 h) and investigate the extraction and stripping stability in time. These stability tests should first be carried out with a synthetic metal solution, and thereafter with a real metal polluted waste water stream to investigate the influence and eventual fate of other compounds present. The next and last step in this research will be the construction and operation of a pilot plant for continuous metal extraction. The following challenges need to be resolved:

Choice of feed solution

First, a selection has to be made of the best metal polluted waste solution to be tested with the continuous metal extraction setup. With the results of chapter 4, it is concluded that the best metal polluted waste water will consist out of one valuable transition metal (Mn, Co, Ni, Cu, Zn) or rare earth metal (La, Nd, Sm, Dy, Er and Yb) in an aqueous solution with other alkali and earth alkaline metals at a pH ranging between 5 and 7.5, from which the transition metal or rare earth metal can be easily separated. This real waste water solution should be first reproduced in the lab (just containing inorganic salts and water) and applied as feed solution in a continuous extraction process in order to investigate the selectivity. The pH and chloride concentration can be adjusted to optimize/maximize the selectivity towards the metal(s) of interest. Next, the real waste water has to be completely analyzed in order to determine all the other (dissolved) solids in the water stream (e.g. clay, organic compounds, biological materials, etc). From literature, it is already know that silica particles will not interact with the IL,[1,2] but the interaction of the IL with clay and other suspended particles has never been investigated. The interaction between the IL and dissolved organic matter is also largely unknown. However, in preliminary experiments it was already observed that humic acids in the water phase were co-extracted into the IL. It is still unknown if this prevent further metal extraction with the IL and if this will have an effect on the selectivity of the IL. In case the dissolved organic matter would have a negative effect on the extraction efficiencies and selectivity, then an additional process should be developed to also remove these organics out of the IL.

Development of pilot-scale continuous metal extraction setup

Oleic acid is sensitive towards oxidation. This can accelerated under influence of light and elevated temperatures.[3] Therefore, to extend the life-time of the IL, the equipment should not be transparent to UV light, and should prevent heat accumulation in the system. Furthermore, in the pilot plant the long-term effect of the interaction between the IL with the plastic tubing's and metal parts should be investigated. Reason is that it is already know that some ILs can dissolve plastics[4] or act as plasticizers[5–7] and dissolve metal oxides,[8,9] but also can protect metal piping from corrosion.[10–12] Engineers will have to select appropriate types of pumps for the high waste water flows consisting of IL-proof construction materials. Stable flow rates are very important, because the velocity of the liquids streams and related to this the contact time between the different solutions determines the efficiency of the system (as indicated in chapter 6). Also, liquid level controllers will have to be placed in the settlers to make sure that the phase disengagement of the IL and aqueous phase occurs in a controlled region (and is less dependent on fluctuations in the feed flows), so that the liquids always have enough time to separate from each other. Additional research has to be performed to minimize the leakage of IL towards the aqueous phase, which leads to the high operational cost of this process. For example, implementation of a hydrophilic filter or membrane unit at the outlet of the feed solution could prevent leakage of the valuable fatty acid based IL towards the water phase.

Regeneration of the IL after metal extraction

Sodium oxalate is now applied as stripping solution in the continuous metal extraction process and results in the formation of a cobalt oxalate precipitate. The formation of a precipitate can be seen as an advantage, because it facilitates its removal from the aqueous phase. However, it can also lead to the blocking of tubes, which indicates that a good design for the mixer-settler at the stripping stage is very important. Regeneration with oxalate will be sufficient for all divalent metal that were tested in chapter 6, because they all form very strong insoluble precipitates with oxalate. But there are metals, like Fe(III), which will form slightly soluble complexes with oxalate and are therefore more difficult to remove from the stripping solution. Recirculation of the stripping solution after filtration to which new sodium oxalate is added may overcome this problem. Running the continuous setup showed that the extraction and stripping reached a stable equilibrium. Therefore, it is expected that an increase in the stripping efficiency will result in a higher continuous extraction efficiency. A possible way to achieve higher stripping extraction efficiencies is to use a multi-stage extractor (e.g., two or more mixer-settlers in series) for the stripping of the IL. Due to the precipitation of the metal oxalates, this will cause no problems related to the further dilution of the end product. Yet, it has to be considered if the higher metal extraction efficiencies outweigh the consumption and cost of additional sodium oxalate and the production of higher volumes of brine solution resulting from the stripping solution.

After separation from the stripping solution, cobalt oxalate complexes (and also other metal oxalate complexes) can be transformed via a process called calcination into their metal oxides.[13] These are valuable products that can be immediately processed in the metallurgical industry. However, this process has to be operated at very high temperatures and also produces a lot of CO_2, which is an important greenhouse gas that mankind nowadays tries to reduce. Also, dewatering and transporting this cobalt precipitate will be costly. Therefore, other sustainable (not to high electrical energy consuming or applying toxic chemicals) regeneration techniques will have to be developed with better stripping efficiencies. An idea for a possible novel regeneration technique was done by an observation in chapter 8. In this chapter electrodialysis (ED) was combined with ILs to in order to minimize water transport and simultaneously obtain highly selective metal extraction. During ED with ILs, the formation of a precipitate was observed at the last cation exchange membrane (CEM) next to the cathode, but also on some parts of the cathode a colour change was observed (see figure 8.7). This is an indication that cobalt was deposited on the cathode during the experiment. From chapter 5 it was know that direct ED of metals out of the IL leads to degradation of the IL, but indirect ED may be a suitable regeneration technology. In this case, the IL would flow in between a CEM and an anion exchange membrane (AEM) that are positioned next to a cathode and anode (see Figure 11.1). The electrolyte between the electrodes and membranes can be water when the metals loaded into the IL can be deposited at a potential where no hydrogen gas and hydroxide formation occurs at the cathode. Other electrolyte media should be applied in case of metals with a higher reduction potential. Indirect electroplating would result in a very stable and compact end product (metal plated on top of the electrode) without consuming additional chemicals. Furthermore, because each metal gets electroplated at a different potential, also an additional separation can be achieved between the different valuable transition metals (Mn, Co, Ni, Cu, Zn,…) that get extracted.

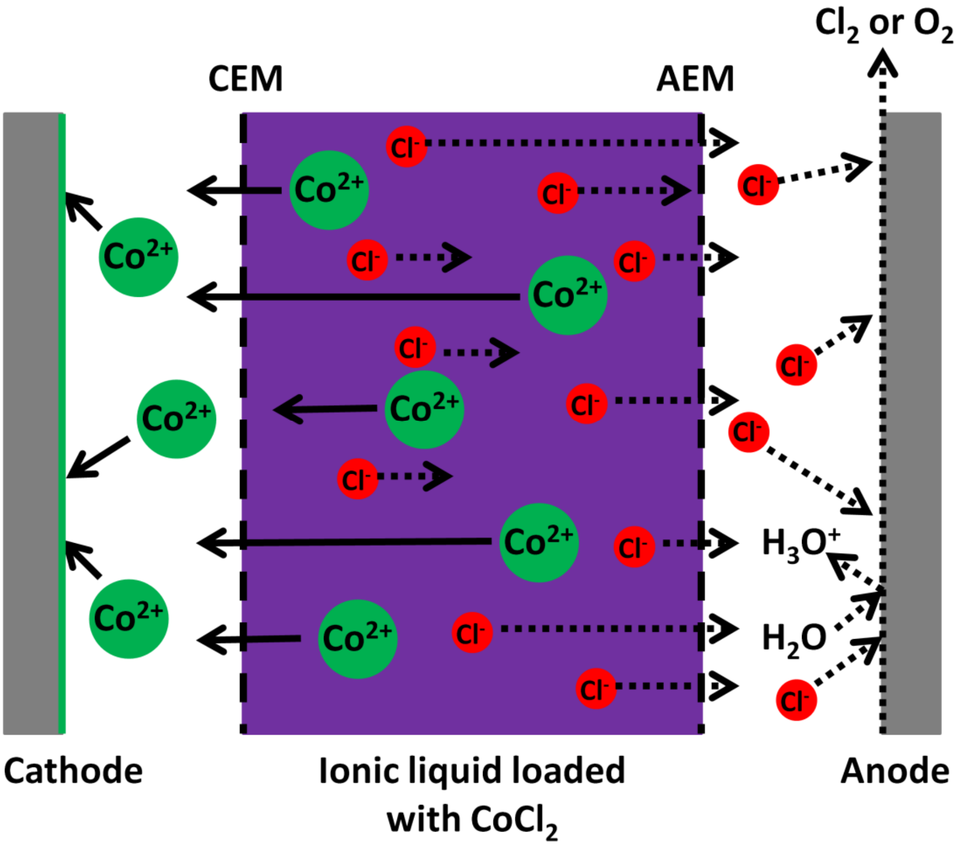

Figure 11.1. *Theoretical idea of indirect electrodeposition with the cobalt chloride loaded ionic liquid and water as electrolyte between the membranes and electrodes. AEM represent the anion exchange membranes and CEM the cation exchange membranes.*

Improvement/intensification of the extraction process

Although simultaneously electrospraying of a metal solution with an IL resulted in an increased separation factor between the transition metals (Mn, Co) and alkaline earth metals (Ca), it is expected that this technology will not be applicable on an industrial scale. Reason for this statement is that for obtaining a stable spraying (cone-jet) mode, a larger volume of the expensive IL is needed to treat the water compared to conventional physical mixing. Also, the flows were too small ($1\ mL\cdot h^{-1}$) to treat large quantities of waste water. Nevertheless, this technology can maybe still find applications in analytical techniques.

In contract to the electrospraying process, it is expected that the electrodialysis (ED) process combined with ILs will be more promising as alternative to conventional ED, because it results into a metal selective ED process and it reduces water transport at the expense of a higher resistance. Still, the problem of precipitate formation at the CEM membrane next to the cathode has to be solved. The effect of this precipitate formation on the metal concentration in the IL will be significantly reduced when the stack will be bigger, but can also be solved by applying a non-aqueous electrolyte solution. Another question that still has to be solved in this process is to find out where the light metals (Na) accumulate in the system. Sodium ions are removed out of the feed/diluate phase by the ED process, but are not extracted into the IL. Compared to the continuous setup, the ED process has similar selectivity but can treat much smaller volumes. Therefore, it is anticipated that physical mixing is the most preferable technique for metal extraction at the industrial scale.

Development of Na selective extraction unit

Because ILs are often called ‘designer solvents’, it is likely that other ILs will be found that are selective for specific metal salts. For example, in this thesis the sodium selective organic ionic crystal $[N_{8888}]$[monensin] was discovered. Next step in this research is to find out why this organic crystal cannot be reused after acidic regeneration, for example via NMR. At this moment, it is assumed that protonation or degradation is preventing the reuse of the organic ionic crystals. In case protonation of the monesin anion is preventing its reuse, other regeneration steps should be developed, e.g. washing with aprotic solvents, regeneration with a base such as LiOH or by applying a potential. If it turns out that the $[N_{8888}]$[monensin] crystal is not stable under acidic conditions, then more stable derivates of monensin should be developed, e.g. by replacing the tetrahydrofuran rings in the monensin structure by more stable tetrahydropyran rings (the 5-atom ring structure of furan is more reactive towards acids due to a higher ring strain compared to 6-atom ring structure of the pyran molecule).

11.3 References

1 C. G. Hogshead, E. Manias, P. Williams, A. Lupinsky and P. Painter, *Energy Fuels*, 2011, **25**, 293–299.

2 P. Painter, P. Williams and A. Lupinsky, *Energy Fuel*, 2010, **24**, 5081–5088.

3 G. Knothe, *Fuel Process. Technol.*, 2007, **88**, 669–677.

4 N. Winterton, *J. Mater. Chem.*, 2006, **16**, 4281.

5 M. P. Scott, C. S. Brazel, M. G. Benton, J. W. Mays, J. D. Holbrey and R. D. Rogers, *Chem. Commun.*, 2002, 1370–1371.

6 M. P. Scott, M. Rahman and C. S. Brazel, *Eur. Polym. J.*, 2003, **39**, 1947–1953.

7 M. Rahman and C. S. Brazel, *Polym. Degrad. Stab.*, 2006, **91**, 3371–3382.

8 A. P. Abbott, G. Frisch, J. Hartley and K. S. Ryder, *Green Chem.*, 2011, **13**, 471.

9 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.

10 N. V. Likhanova, M. A. Domínguez-Aguilar, O. Olivares-Xometl, N. Nava-Entzana, E. Arce and H. Dorantes, *Corros. Sci.*, 2010, **52**, 2088–2097.

11 N. Birbilis, P. C. Howlett, D. R. MacFarlane and M. Forsyth, *Surf. Coatings Technol.*, 2007, **201**, 4496–4504.

12 Q. B. Zhang and Y. X. Hua, *Electrochim. Acta*, 2009, **54**, 1881–1887.

13 I. Luisetto, F. Pepe and E. Bemporad, *J. Nanoparticle Res.*, 2008, **10**, 59–67.

Summary

The scope of this thesis was to investigate if it is possible to demineralise/desalinate water using ionic liquids (ILs) as extractants for selective salt extraction. ILs are organic salts that are liquid at room temperature. Because ILs solely consist out of ions, they are excellent in stabilizing other charged species, such as metals dissolved in the water phase. The concept of applying ILs for demineralisation/desalination is based on the more energetically desirable selective removal of minority compounds (salt) from the saline water stream. This in contrary to the most common desalination technique, such as reverse osmosis and thermal desalination, which remove the majority compound (water) from the saline stream.

Several hydrophobic fatty acid based ILs were selected for metal extraction and developed in order to prevent and minimize the pollution of the treated aqueous phase with toxic organics. Their synthesis was simple and first metal extraction tests with these ILs showed no or negligible extraction efficiencies for alkali metal (Li, Na, K) salts, but very good extraction efficiencies were observed for the period IV transition metal (Mn, Fe, Zn) salts. Furthermore, the extraction mechanism was based on ion-pair extraction and not on ion-exchange, preventing loss of valuable IL ions into the aqueous phase.

Determination of the extraction mechanism of these liquids for the transition metal ions Co(II), Ni(II) and Zn(II) learnt us that both the anion and the cation of the IL tetraoctylammonium oleate ($[N_{8888}^{+}][oleate^{-}]$) can stabilize the metal ion. The metals Co(II) and Ni(II) were stabilized via a $[N_{8888}^{+}][M(oleate)_3^{-}]$ complex. Zn(II) was extracted via a different extraction mechanism, in which the Zn(II) ion was stabilized as a $ZnCl^{+}$ ion in an IL metal complex, i.e. $[N_{8888}^{+}]_2\left[MCl_2(oleate)_2{}^{2-}\right]$ at the applied conditions. The presence of a very stable chloride ligand in the case of Zn compared to the oleate ligand resulted in the higher distribution ratio for Zn compared to Ni and Co.

The HCl acid concentration (and thus the chloride concentration and pH) was found to have a large influence on the extraction efficiency with the fatty acid based IL. Investigation of the extraction efficiencies as function of the pH for different metals (Li, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, In, La, Nd, Sm, Dy, Er, Yb) indicated that all metals have an optimal pH at which they can be extracted. Full extraction of Na and K was not possible, due to the formation of an emulsion agent, i.e. Na or K oleate at higher pH values. The transition metals Mn, Co and Ni were extracted via the anion of the IL at a pH of 6–7, while all rare earths were extracted from the solution at a pH of 5–6. This means that there is a pH difference of

one unit between these metals, which shows that the fatty acid based IL 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 were extracted as anionic chloro complex via the cation of the IL at low pH.

Preferably, regeneration of the fatty acid based ILs after metal extraction was done via electrodeposition, because then no additional chemicals have to be added to the system. Unfortunately, this was not feasible due to the high resistance and viscosity of the IL. Furthermore, degradation of the IL occurred in the presence of oxygen. Alternatively, chemical regeneration via a 0.1M sodium oxalate solution was selected as most suitable technique to strip the metals from the IL without preventing its posterior reuse. Strong acids and bases were also able to remove all the metals from the IL, but then direct reuse of the IL was not possible due to the protonation of the anion of the IL (in case acids were used) or due to the formation of the emulsifying agent Na oleate (in case bases were used).

The IL tetraoctylphosphonium oleate ($[P_{8888}]$[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 in a continuous process for selective metal extraction. It was shown that this IL has a relatively low viscosity due to the solubility and uptake of water, which is mainly related to the anion of the IL. Operating the continuous setup with a Ca/Co/K feed stream for 5 h proved that this setup is able to selectively extract metals in a continuous mode to obtain a cobalt stream with traces of calcium and no potassium. During this experiment, it was also noticed that the contact time of the IL for extraction and stripping determined the achieved efficiencies. Furthermore, it was demonstrated that the fatty acid based IL was stable for the duration of the experiment. Economical analysis showed that the continuous process for metal extraction based on ILs compared to ion-exchange resins is a very promising alternative for selective metal removal in combination with the recovery of the valuable extracted metals.

It was also investigated if combining existing desalination technologies with the new fatty acid based ILs could result in an improvement of the continuous metal extraction process. First, it was analyzed if electrospraying the IL together with an aqueous metal phase through a coaxial nozzle could result in an enhanced metal extraction efficiency. Results showed that electrospraying did not result in an improvement of the extraction efficiency. Yet, the selectivity towards the valuable transition metals over light metals increased.

Electrodialysis (ED) was also operated with a hydrophobic metal selective IL as concentrate phase. This resulted in a reduced water transport towards the concentrate phase and prevented leakage of the IL towards the treated water phase. The removal ratio of ions out of the diluate phase depended solely on the ED process, but the uptake of ions into the concentrate phase depended strongly on the selectivity of the IL. It was concluded that this type of ED was promising to selectively extract transition metals from an aqueous phase and to concentrate them.

As a side project in this research, it was also tried to develop a sodium selective IL based on the ionophore monensin. After the synthesis ionic crystals were obtained that were highly selective for sodium. Regeneration of this ionic crystal was possible by applying acidic solutions. However, the reuse of the ionic crystal was limited.

Nederlandse Samenvatting

Het doel van deze thesis was de mogelijkheid onderzoeken om water te demineraliseren/ontzouten met ionische vloeistoffen (ILs) als extractants voor selectieve metaal extractie. ILs zijn organische zouten die vloeibaar zijn bij kamertemperatuur. Omdat ILs alleen maar bestaan uit ionen kunnen ze heel goed andere geladen deeltjes stabiliseren, zoals metalen opgelost in de water fase. Het concept voor het gebruik van ILs voor demineralisatie /ontzouting is gebaseerd op het feit dat het energetisch gunstiger is om de kleinste component (zout) te verwijderen uit zout water. Dit is het tegenovergestelde van de huidige meest gebruikte ontzoutings technieken, zoals reverse osmose en thermische ontzouting. Deze verwijderen de grootste component, namelijk water, van het zout water.

Verschillende hydrofobe vetzuurgebaseerde ILs werden geselecteerd en ontwikkeld om te vermijden dat de behandelde waterfase zou vervuild worden met toxische organische moleculen. De gebruikte synthese was simpel en de eerste metaalextractie testen toonden aan dat deze ILs alkali metalen (Li, Na, K) zouten niet of maar weinig extraheerden. Terwijl heel goede extractie efficiënties werden waargenomen voor de periode IV transitie metaalzouten (Mn, Fe en Zn). Verder was het extractiemechanisme gebaseerd op ion-paar extractie en niet op ion-uitwisseling, wat het verlies van de waardevolle IL voorkomt.

Determinatie van het extractie mechanisme van deze vloeistoffen voor de transitiemetalen Co(II), Ni(II) en Zn(II) leerde ons dat zowel het anion als het cation van de IL tetraoctylammonium oleate ($[N_{8888}^{+}][oleate^{-}]$) het metaalion kan stabiliseren. De metalen Co(II) en Ni(II) werden gestabiliseerd via een $[N_{8888}^{+}][M(oleate)_3^{-}]$ complex. Zn(II) was geëxtraheerd via een verschillend extractiemechanisme, in welke het Zn(II) ion werd gestabiliseerd als een $ZnCl^{+}$ ion in een IL metal complex, i.e. $[N_{8888}^{+}]_2\left[MCl_2(oleate)_2{}^{2-}\right]$ bij toegepaste condities. De aanwezigheid van een zeer stabiel chloride ligand in het geval van het metaal complex met Zn vergeleken met het oleate ligand resulteerde in de hogere distributie verhouding voor Zn vergeleken met Ni en Co.

Tijdens het onderzoek werd opgemerkt dat de HCL zuurconcentratie (en dus de chloride concentratie en pH) een grote invloed heeft op de extractie efficiëntie van de vetzuur gebaseerde IL. Een studie in verband met de extractie efficiëntie als een functie van de pH voor de verschillende metalen (Li, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, In, La, Nd, Sm, Dy, Er, Yb) toonde aan dat alle metalen een optimale pH hebben bij welke extractie plaatsvindt. Volledige extractie van Na en K was niet mogelijk vanwege de vorming van een surfactant, i.e. Na of K oleate bij hogere pH waardes. De transitie metalen Mn, Co en Ni werden geëxtraheerd via het anion van de IL bij een pH van 6-7, terwijl alle zeldzame aard metalen werden geëxtraheerd van de oplossing bij een pH van 5-6. Dit betekent dat er een pH verschil van één eenheid tussen deze metalen is, wat aantoont dat de vetzuurgebaseerde IL een potentiële kandidaat is voor de scheiding van transitiemetalen van zeldzame aardmetalen. De metalen Zn, Cu, Fe en In kunnen gescheiden worden van de zeldzame aard metalen bij een pH < 5, omdat deze metalen worden geëxtraheerd als anionische chloro complexen via het cation van de IL bij een lage pH.

Theoretisch gezien was de best geschikte regeneratie voor de ILs na metaal extractie electrodepositie, omdat er dan geen extra chemicaliën moeten toegevoegd worden aan het systeem. Jammer genoeg was dit niet mogelijk door de hoge weerstand en viscositeit van de IL. Daarnaast gebeurde er ook nog degradatie van de IL in de aanwezigheid van zuurstof. Als alternatief werd chemische regeneratie via een 0.1 M natrium oxalate oplossing geselecteerd als meest geschikte techniek om de metalen terug uit de IL te halen zonder het hergebruik ervan te limiteren. Sterke zuren en basen konden ook alle metalen uit de IL terugwinnen, maar direct hergebruik van de IL was niet mogelijk door de protonatie van het anion van de IL (in het geval zuren werden gebruikt) of door de vorming van de surfactant Na oleate (in het geval basen werden gebruikt).

In een volgende fase van mijn onderzoek werd de IL tetraoctylphosphonium oleate ([P_{8888}][oleate]) gebruikt in zijn onverdunde vorm als zowel de organische fase als de extractie agent voor de selectieve terugwinning van chloor metaalzouten uit een waterige oplossing in een continue extractie opstelling. Er werd aangetoond dat deze IL een relatief lage viscositeit heeft door de opname van water, wat vooral gerelateerd is aan het anion van de IL. Deze extractie opstelling werd voor 5 uren in werking gesteld met een Ca/Co/K startoplossing en toonde aan dat het mogelijk is om continu selectief metalen te extraheren. Gedurende dit experiment werd het duidelijk dat vooral de contacttijd van de IL in de extractie- en regeneratiestap de behaalde extractie-efficiency beïnvloedde. Verder werd er ook aangetoond dat de vetzuurgebaseerde IL stabiel was voor de volledige duur van het experiment. Een economische analyse van het proces voor continue metaalextractie gebaseerd op ILs, vergeleken met ionwisselaarhars, toonde aan dat deze techniek een veelbelovend alternatief is voor de selectieve verwijdering van metalen in combinatie met de terugwinning van deze waardevolle geëxtraheerde metalen.

We onderzochten ook of ILs gecombineren met bestaande ontzoutings technieken kan resulteren in een verbetering van de bestaande processen. Eerst werd er onderzocht als electrospraying van de IL samen met de waterige metaal oplossing door twee coaxiale naalden kan leiden tot een verbeterde metaalextractie. Elestrospraying resulteert in een heel korte contact tijd waarbij het toegepaste elektrisch veld metaalextractie bevordert. Resultaten toonden aan dat dit niet resulteerde in een verbetering van de extractie efficiency vergeleken met het conventionele mechanisch mixen. Er werd echter wel een betere selectiviteit voor de waardevolle transitiemetalen waargenomen ten opzichte van de lichte metalen.

De hydrofobe metaalselectieve IL werd ook geïntroduceerd als de fase waarin metalen worden geconcentreerd in het electrodialyse (ED) proces. Dit resulteerde in een verminderd watertransport naar de concentratie fase en vermijd dat er IL lekt naar de waterfase. De verwijderingsnelheid van de metaalzouten was volledig afhankelijk van het ED proces, maar de opname van ionen in de concentratiefase is afhankelijk van de selectiviteit van de IL. Er werd geconcludeerd dat dit type van ED proces veelbelovend is voor het selectief extraheren van metalen uit de waterige fase en deze op te concentreren.

Als zijproject in dit onderzoek werd er geprobeerd om een natriumselectieve IL te ontwikkelen gebaseerde op de ionofoor monensin. Na de synthese werden er ionische kristallen bekomen die zeer selectief zijn voor natrium. Regeneratie van dit kristal is mogelijk door het gebruik van een zure oplossing. Jammer genoeg verhindert dit het hergebruik van de ionische kristallen.

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While finalizing this thesis I realize that I’m closing down a chapter in my life. It was an exciting period of 4 yours of my life that passed by so quickly. I hope that in this period, I made a contribution to the society to evolve in a more circular economy. In which valuable resources (water and metals) can be more and more recovered. But I could not do this huge amount of work that is being compressed in this thesis all by myself. It is a work in which many people contributed from the start until the end.

First of all, I would like to thank my parents and family for their support during my studies. Although my tutors in primary and secondary school each time told me that I was aiming to high for my next education, you always believed in me. Telling me that “even with a small pony you can win the steeple race as long as you work hard”. I had my tuff moment, especially when I saw that the people in my surrounding were picking up so easily new knowledge. Yet at the end, this period contributed a lot to the person that I am now. From which I feel myself connected with people like Ir. Dirk Frederik Wouda whose aphorism is written on the Woudagemaal: "Wie slagen wil, die slagen kan". Also special thanks to Zr. Maria Bosco and Zr. Maria Victor who helped me in the beginning of my studies via private lessons with French and mathematics and later on for their support and blessings.

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Wetsus, what a nice place to work! I liked the independency and responsibility that you get in managing your own PhD and the easiness to cooperate with other researchers from other scientific fields. Cees and Johannes, I admire you for what you have achieved and I hope that Wetsus can further contribute to many novel techniques that can be implemented in the water sector.

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Curriculum Vitae

Dries Parmentier was born on 11-7-1987 in Waregem, Belgium. After finishing technical secundair eduction (TSO) in 2005 at Sint-Vincentiusinstituut in Anzegem, Belgium, he studied chemistry at the Katholieke Universiteit Leuven, Belgium. In 2011 he graduated within the LIC research group of Prof. Dr. Koen Binnemans under the supervision of Lethesh Kallidanthiyil Chellappan on the subject: ”Anion exchange in ionic liquids via the phenolate platform”. From November 2011, he started a PhD project guided by the Technical University of Eindhoven and performed at Wetsus, European centre of excellence for sustainable water technology located in Leeuwarden, The Netherlands. The results obtained during his PhD are presented in this dissertation. In 2014, he has been awarded the annual Marcel Mulder prize for his important contribution to the development of ionic liquids desalination technology.

List of publications

-Parmentier, D., Metz, S.J. and Kroon, M.C. (2013). Tetraalkylammonium oleate and linoleate based ionic liquids: promising extractants for metal salts. *Green Chemistry*, *15*(1), 205-209

-Parmentier, D., vander Hoogerstraete T., Valia, Y. A., Metz, S. J., Binnemans, K and Kroon, M.C. (2015). Mechanism for extraction of first row transition metals from chloride media with the ionic liquid, tetraoctylammonium oleate. *Under progress*

-Parmentier, D., vander Hoogerstraete T., Valia, Y., Metz, S. J., Binnemans, K and Kroon, M.C. (2015). Selective extraction of metals from chloride solutions with the tetraoctylphosphonium oleate ionic liquid. *Ind. Eng. Chem. Res.*, 2015, 54 (18), pp 5149–5158

-Parmentier, D., Valia Y.A. , Metz S.J. , Burheim O.S. and Kroon, M.C. (2015), Regeneration of the ionic liquid tetraoctylammonium oleate after metal extraction. Accepted for publication in *Hydrometallurgy*.

-Parmentier D., Rybałtowska A., van Smeden J., Kroon M.C. and Lemos L. (2015) Electrohydrodynamic atomization of ionic liquids as a tool to enhance the extraction of metallic salts. Accepted for publication in *Journal of Electrostatics*.

-Parmentier D., Vilar S. P., Metz S.J., Wiedmer S.K. and Kroon, M.C., Continuous setup for selective metal extraction with the ionic liquid tetraoctylphosphonium oleate. Submitted to *Chemical Engineering Journal.*

-Parmentier, D., Galama, O., Nowak, M., Metz, S. J., and Kroon, M.C. Investigation of the electrodialysis process in combination with the tetraoctylphosphonium oleate ionic liquid as concentrate stream. Submitted to *Purification and Separation technology*

-Parmentier, D., Lavenas, M., Güler, E., Metz S.J., and Kroon, M.C., Selective removal of sodium with tetraoctylammonium monensin. Submitted to *Ion Exchange and Solvent Extraction.*

Prizes

-Oktober 2014, Marcel Mulder Prize, Leeuwarden, The Netherlands

-September 2015, Poster Prize on the first IWA resource recovery congress, Gent, Belgium.