IONIC LIQUID-BASED METAL RECOVERY

FROM AQUEOUS INDUSTRIAL
PROCESS AND WASTE STREAMS

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To my beloved husband, son and parents

SUMMARY

One of the EU's strategies to combat climate change is the transition toward low-carbon energy technologies such as the transition to electric vehicles (EV's). The accelerated introduction of EVs increases the demand for lithium-ion batteries (LIBs), where Cobalt (Co) supply is expected to be the bottleneck in their production. Co is one of the most critical raw materials on earth due to its rare existence and its near-monopolistic supply structure. Therefore, there is a growing incentive, if not critical need, for recycling Co from different waste sources such as industrial wastewater streams and spent LIB's leachate. Although the process of Co retrieval plays an important role in replenishing Co stockpiles, it also contributes to reducing the environmental impact of industrial Co use and reducing the reliance on Co mining, during which the miners are exposed to highly hazardous conditions.

Liquid-liquid extraction (LLX) is one of the most widely applied hydrometallurgical techniques for metal separation and recovery. LLX is defined as the migration of a solute from the feed into a solvent, followed by back-extraction to retrieve the end product and reuse the solvent. It allows efficient processing of large volumes of aqueous solution in a continuous mode with relatively low capital and operational costs. At the beginning of the 21st century, a new type of solvents, known as ionic liquids (ILs), found their way to scientists. These liquids, defined as salts which is in the liquid state at ambient temperatures or below 100 °C, have interesting properties such as a negligible vapor pressure, high thermal stability and a wide liquidus temperature range. ILs are often described as designer solvents and green alternative solvents because of their ability to fine-tune their structure-function relationship and negligible vapor pressure, respectively. Compared to conventional volatile organic compounds (VOCs), ILs are also considered to be a safer alternative due to their low flammability. However, a serious issue related to the application of some ILs is their solubility in aqueous media, which might lead to a pollution threat for the aquatic environment. Although, this is not true for all ILs, the application of each individual IL should be thoroughly checked for this aspect, even more so if one or more of the IL components is considered to be rather toxic.

In this PhD thesis, several aspects of process upscaling of an IL-based LLX system are considered. The goal is to investigate the application of an IL-based LLX process for the extraction and recovery of different transition metals (notably Co) from different process streams. In order to achieve this, fundamental research, experiments, modelling and a preliminary economic analysis are all included. It is decided to use tetraoctylphosphonium oleate [P_{888}^+][Oleate] as the solvent due to its unique selectivity towards transition metals. This makes it a good candidate for the extraction of Co from industrial wastewater and spent synthetic LIB leachate. First, the LLX process is investigated at lab-scale in **Chapter 2**

to recover Co from a chloride-based aqueous medium. Extraction-regeneration processes are followed for five consecutive cycles using $[P_{888}][\text{Oleate}]$ as the solvent and aqueous Na_2CO_3 solutions for regeneration. The main criteria to evaluate the feasibility of any potential application of ILs are the following: the extraction efficiency, the recovery and the loss of the IL and the production of commercial valuable end-product.

In **Chapter 3**, the IL $[P_{888}][\text{Oleate}]$ is applied to selectively extract and recover valuable metals (Co, Ni, Mn and Li) from synthetic leachates resembling those from spent lithium-ion battery cathodes, under different conditions. The parameters investigated for this selective separation and recovery process include the extraction pH, contact time, composition of the regeneration solutions and number of required extraction/regeneration stages within one cycle. Additionally, an economic potential analysis (EP0) is performed to evaluate the commercial feasibility of the proposed process.

In **Chapter 4**, we address a number of questions regarding IL-based metal extraction at the more fundamental level. These questions relate to the metal affinity, extraction mechanism and the effect of presence of inorganic anions and cations other than Co in the aqueous phase. The selection of the extraction mechanism eventually considered as most adequate is based on: (1) model fitting of the extraction isotherms as obtained at different temperatures, (2) evaluating different thermodynamic parameters, including equilibrium constant, Gibbs energy, enthalpy, and entropy of the complexation reaction and (3) analysing the physical properties of the LLX system such as the change in viscosity and electric conductivity.

In **Chapter 5**, a LLX process is performed using a single droplet extraction column. The aim of these experiments is, first, to investigate the mass transfer of Co from water to IL droplets in more details, secondly, to identify the mass transfer limitation, and finally, to estimate the mass transfer and kinetic parameters. This investigation evaluates various mass transfer models, with(out) a chemical reaction using a statistical cross-validation method (CV_5). The outcome of the CV_5 analysis, includes the effect of column length, droplet diameter, droplet rising velocity (and thus contact time) and the Co concentration in the continuous and dispersed phases on Co uptake.

Chapter 6 discusses, the extraction of Co by $[P_{888}][\text{Oleate}]$ using a laboratory scale KARR® reciprocating plate extraction column. The influence of different operating variables on the performance of the column are evaluated; these variables are the frequency of agitation and the flow rates of the solvent and the aqueous phase. Moreover, experiments are performed to study the effect of the solvent-to-feed ratio on the hydrodynamic performance of the column and the ratio at which flooding is likely to occur. Additionally, a mathematical model using literature correlations for mass transfer, holdup and droplet

diameter is developed. The results from this model are compared to the experimental data obtained in this study as well as those reported in literature.

Finally, it is concluded that the IL [P₈₈₈₈][Oleate] shows a good potential for the extraction and recovery of valuable transition metals due to its selectivity towards the targeted metals. However, the main drawback when performing the LLX process in a laboratory scale extraction column (KARR[®]) is the need for the addition of a substantial amount of diluent to avoid flooding, which narrows the window of operation due to the limited IL/feed ratio and accordingly lowers the extraction efficiency.

SAMENVATTING

Een van de strategieën van de EU om klimaatverandering tegen te gaan, is de overgang naar koolstofarme energietechnologieën, zoals de overgang naar elektrische voertuigen (EVs). Door de versnelde introductie van elektrische voertuigen neemt de vraag naar lithium-ion batterijen (LIBs) toe waarbij de aanvoer van kobalt (Co) naar verwachting de bottleneck zal vormen bij hun productie. Co is een van de meest kritische grondstoffen vanwege de beperkte beschikbaarheid en de bijna monopolistische toeleveringsstructuur. Daarom is recycling van Co uit verschillende afvalbronnen, zoals industriële afvalwaterstromen en gebruikt LIBs percolaat, cruciaal. Hoewel het proces van Co-terugwinning een belangrijke rol speelt bij het aanvullen van de Co-voorraad, is het even zo belangrijk om de milieu-impact van industrieel Co-gebruik te verminderen, evenals de verschrikkelijke werkomstandigheden tijdens Co-winning uit mijnen.

Vloeistof-vloeistofextractie (liquid-liquid extractie of LLX) is een van de meest toegepaste hydrometallurgische technieken voor metaalscheiding en terugwinning uit waterige stromen. Het wordt gedefinieerd als het overdragen van een opgeloste stof uit de originele oplossing naar een oplosmiddel, gevolgd door verwijdering als eindproduct uit het oplosmiddel waarmee tevens hergebruik van het oplosmiddel mogelijk is. Het maakt continue en efficiënte verwerking van grote hoeveelheden waterige oplossing mogelijk met relatief lage kapitaal- en operationele kosten. In het begin van de 21^{ste} eeuw werd een nieuw type extractiemiddelen geïntroduceerd, genaamd ionische vloeistoffen (ILs). Deze vloeistoffen, gedefinieerd als zouten met een smeltpunt lager dan 100°C, hebben interessante eigenschappen zoals een verwaarloosbare dampspanning, hoge thermische stabiliteit en zijn vloeibaar over een breed temperatuurbereik. IL's worden vaak bestempeld als designer-oplosmiddelen en als groene alternatieve oplosmiddelen vanwege de mogelijkheid om hun eigenschappen te tunen en hun verwaarloosbare dampspanning. In vergelijking met conventionele vluchtige organische stoffen (VOS), worden ILs ook als een veiliger alternatief beschouwd vanwege hun lage ontvlambaarheid. Een belangrijk probleem met betrekking tot het gebruik van sommige ILs is echter hun oplosbaarheid in water, wat kan leiden tot waterverontreiniging en daarmee tot een bedreiging voor het aquatisch milieu. Hoewel dit misschien niet in elk systeem wordt waargenomen, moet het worden gecontroleerd en voorkomen.

In dit proefschrift worden verschillende aspecten van opschaling behandeld om de toepassing van op IL-gebaseerde LLX-processen te onderzoeken voor de extractie en terugwinning van transitie-metalen, voornamelijk Co, uit verschillende processtromen. Dit wordt bereikt door een combinatie van fundamenteel onderzoek, experimenten, modellering en een voorlopige economische analyse. Voor dit doel wordt het IL-

tetraoctylfosfoniummoleaat [P_{8888}][Oleate] geselecteerd als extractiemiddel vanwege onder ander zijn unieke selectiviteit voor transitie-metalen, waardoor het een goede kandidaat is voor de extractie van Co uit industrieel afvalwater en synthetisch LIB-percolaat.

Allereerst wordt in **Hoofdstuk 2** het LLX-proces op lab-schaal onderzocht om Co terug te winnen uit een waterige chlorideoplossing. Extractie-regeneratieprocessen worden uitgevoerd gedurende vijf opeenvolgende cycli gebruikmakend van [P_{8888}][Oleate] als extractiemiddel en Na_2CO_3 opgelost in water als regeneratieoplossing. De belangrijkste criteria om de haalbaarheid van een mogelijke toepassing van ILs te beoordelen, worden gedefinieerd op basis van de extractie-efficiëntie en de terugwinning van het Co, het verlies van de IL en het verkrijgen van een waardevol eindproduct.

In **Hoofdstuk 3** wordt de IL [P_{8888}][Oleate] toegepast om selectief waardevolle metalen (Co, Ni, Mn en Li) te extraheren en terug te winnen uit synthetisch percolaat afkomstig van het recyclen van gebruikte LIB kathodes. Verschillende parameters voor dit selectieve scheidings- en terugwinningsproces worden onderzocht, zoals de extractie-pH, contacttijd, samenstelling van de regeneratieoplossingen en het aantal vereiste extractie-regeneratiestappen binnen één cyclus. Daarnaast wordt het economisch potentieel (EP0) geanalyseerd om de haalbaarheid van het voorgestelde proces te evalueren.

In **Hoofdstuk 4** wordt ingegaan op belangrijke, meer fundamentele vragen op het gebied van metaalextractie met behulp van ionische vloeistoffen (ILs) zoals de metaalaffiniteit, het extractiemechanisme, het effect van anorganische anionen en kationen in de waterige fase. Het voorgestelde extractiemechanisme van Co met behulp van dit IL wordt gebaseerd op (1) het modelleren van de extractie-isothermen verkregen bij verschillende temperaturen, (2) het evalueren van verschillende thermodynamische parameters, waaronder evenwichtsconstante, Gibbs-energie, enthalpie en entropie van de complexeringsreactie, en (3) het analyseren van de fysische eigenschappen van het LLX-systeem, zoals de verandering in viscositeit, elektrische geleidbaarheid en activiteit.

In **Hoofdstuk 5** wordt het LLX-proces uitgevoerd in een druppelextractie-kolom om de stofoverdracht van het Co uit water naar IL-druppels te onderzoeken en om de snelheidsbeperkende stofoverdrachtstrap te identificeren. Verschillende stofoverdracht modellen, met en zonder een chemische reactie, worden geëvalueerd met behulp van een statistische methode waarbij het resultaat het effect omvat van kolomlengte, druppeldiameter, stijgensnelheid van druppels en continue en gedispergeerde faseconcentraties op Co-opname.

Hoofdstuk 6 behandelt de extractie van Co met behulp van [P_{8888}][Oleate] en gebruikmakend van een op lab-schaal uitgevoerd in KARR[®] extractiekolom. De invloed

van verschillende variabelen op de prestaties van de kolom worden geëvalueerd, inclusief de pulsatiefrequentie, de stroomsnelheden van het oplosmiddel en de waterfase. Bovendien worden verschillende experimenten uitgevoerd om te bestuderen in hoeverre de verhouding van oplosmiddel tot voedingsdebiet de hydrodynamische prestatie van de kolom beïnvloedt zonder flooding te veroorzaken. Daarnaast wordt een wiskundig model ontwikkeld op basis van literatuurcorrelaties voor massaoverdracht, hold-up en druppeldiameter. De resultaten van dit model worden vergeleken met de experimentele resultaten die in deze studie werden verkregen, evenals die gerapporteerd in de literatuur.

Ten slotte wordt geconcludeerd dat de IL [P₈₈₈₈] [Oleate] een goed potentieel vertoont voor de extractie en terugwinning van waardevolle transitie-metalen vanwege zijn selectiviteit voor de beoogde metalen. Het belangrijkste geconstateerde nadeel bij het uitvoeren van het LLX-proces in een laboratoriumschaal extractiekolom (KARR®) is echter de noodzakelijke toevoeging van een substantiële hoeveelheid oplosmiddel om flooding te voorkomen. Het toevoegen van dit oplosmiddel verkleint het werkvenster vanwege de beperkte hoeveelheid IL die ingezet kan worden relatief tot het voedingsdebiet en dienovereenkomstig de extractie-efficiëntie verlaagt.

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CHAPTER 1

INTRODUCTION

Everything is theoretically impossible until it is done

Robert A. Heinlein

BACKGROUND

The biggest challenge facing humanity in the coming century is coming up with solutions to combat global warming. One such approach is through research and development toward low-carbon energy technologies. Although Carbon dioxide (CO₂) has the lowest global warming potential of all greenhouse gases and a relatively short life-time in the atmosphere, CO₂ has had the greatest impact on the environment as it forms almost 80% of all GHGs emissions [1, 2]. In 2020, the Mauna Loa Observatory in Hawaii reported that the average CO₂ level in the atmosphere exceeds the 400 ppm level, which represents an increase of more than 40% since the industrial revolution and the highest value over the past 650,000 years [3]. This triggered the European Union (EU) to formulate the climate-neutral vision, which aims to create zero net GHGs emissions by 2050. This vision involves all economic sectors, from energy production to industry, mobility, buildings, agricultural and forestry sectors [4]. Working towards net zero GHGs emission could be achieved by substantially reducing the dependence of mobility on fossil fuels and a transition to the use of clean, sustainable and renewable energy sources. Since conventional road transport is responsible for approximately 12% of the global GHGs emissions (Figure 1.1) and 12% of the total EU emission of CO₂, one would expect that one of the major goals of the 2050 vision is the transition to cars fully powered by renewable energy sources such as electric vehicles (EV's) [5]. However, unfortunate limitations that make this transition more complicated are the high technology costs, scarcity of desired raw metals and the challenge of establishing a charging infrastructure. Bernstein's research team, a well-known Wall Street research firm, has predicted that in 20 years electric vehicles are going to represent around 40 percent of the 100 million vehicles produced and sold annually once the aforementioned challenges are overcome [6]. This "electric revolution" is also driven by government policies in countries such as France and Britain that will ban fossil fuel-powered vehicles from their roads by 2040 [6].

Figure 1.1: Global greenhouse gas emissions by sectors in 2016 [7].

The accelerated introduction of EVs increases the demand for the lithium-ion battery (LIB). However, a potential bottleneck in the deployment of LIBs may be the supply of cobalt (Co), which has been identified as a critical raw material by the European Commission due to its high supply risk and economical value [8]. The main reasons behind the high supply risk are the extremely rare existence of Co on earth and the prevalence of near-monopolistic supply structures where 59% of the global supply is sourced from mines in the Democratic Republic of Congo [9]. In addition, Co is considered one of the most valuable raw materials in supporting economic growth and development due to its wide uses in industrial applications, ranging from aircraft engines, rechargeable batteries, paints, coatings and catalysts [10, 11]. The expected deficit of Co in 2030 is estimated to be 149000 tonne/year which is mainly caused by the growing demand of portable electronics and the revolution of electric vehicles as shown in Figure 1.2 [12]. Therefore, there is a critical need for recycling Co from different waste sources such as industrial wastewater streams and spent LIB's leachate. This could play an important role in establishing a functioning circular economy, especially in the current context of diminishing metal reserves worldwide [13]. Apart from environmental issues, the additional bonus of this approach is that waste streams are turned into resources of valuable elements.

Figure 1.2: Global refined cobalt supply and demand in tonnes per year (source: BNEF) [12].

1.1 COBALT RECOVERY FROM PROCESS STREAMS

Industrial wastewater streams containing Co are produced from various industries such as electroplating and manufacturing plants of rechargeable battery, electronics, catalysts, ink and pigments and alloys (superalloys, wear-resistant alloys and magnetic alloys) [14, 15]. For example, the waste stream arising from a cobalt/nickel plating bath contains around 5 g/L Co where the maximum allowable limits for wastewater disposal, for a common discharge from electroplating metal industries of more than 38000 L/day, is 4 mg/L for each metal according to the electronic code of federal regulations (e-CFR) [15, 16]. Assuming 90% Co recovery, this could result in a production of 62 tons Co/year. This amount might be economically still modest given the aforementioned deficit, it is vital to reduce the negative impact of Co and other heavy metals on the environment and health care. Furthermore, the recovery of heavy metals can turn wastewater from an expensive burden into a source of revenue while closing the supply chain loop for these industries.

On the other hand, the recycling of electric vehicles batteries (i.e., lithium ion battery) will create an alternative Co supply, thereby increasing its availability and supply security. Figure 1.3 represents the number of batteries available for recycling based on the average number of batteries deployed in each of the International Energy Agency (IEA) scenarios

[8]. The number of batteries is estimated in the period between 2018- 2030, assuming that these batteries reach end of life after 8 years, i.e., end of first use, and become potentially available for recycling [8]. Additionally, it is assumed that 90 % of all batteries deployed worldwide will be collected and subsequently recycled [8]. It is reported by the European Commission that the estimated average Co content per electric vehicle is 5.5 kg in 2017 [8]. It is expected that this amount will double in 2030 to match the projected growths in the storage capacity of electric vehicle batteries [8]. Figure 1.3 shows the estimated amount of recycled Co as well, assuming 90% recovery efficiency. This rough estimation shows that the recovery of Co, which can be more than 66000 ton in 2030, may form a potential secondary source and will compensate almost 50% of the expected deficit discussed earlier.

Figure 1.3: Number of batteries from electric vehicle (BEV) potentially available for recycling until 2030, would-wide and in the EU, and the estimated annual amount of Co recovered assuming a 90% recovery efficiency, given a Co content of either 5.5 or 11 kg/ battery [8].

1.2 CONVENTIONAL METAL RECOVERY TECHNOLOGIES

Various techniques for the separation of metals from aqueous solutions are described in the literature. These technologies are based on physicochemical methodologies and include chemical precipitation, coagulation-flocculation, flotation and cementation. Additionally, adsorption onto zeolites, clay and ion exchange resin and membrane filtration techniques such as ultrafiltration, nanofiltration and reverse osmosis have also been described [14, 17-20].

1. **Chemical precipitation:** This is an important industrial process and one of the earliest technologies employed to remove heavy metals from inorganic effluents [14, 18]. The desired element precipitates by supersaturating the desired solute. The conceptual mechanism of chemical precipitation for metal removal can be defined as the following [21]:

Where M^{2+} , OH^- and $M(OH)_2$ represent the metal ions, precipitant and insoluble metal precipitate, respectively. Lime and limestone are the most commonly used precipitant agents due to their availability and low cost [14, 22, 23]. Lime precipitation can be effectively used to remove heavy metals from acidic metal-containing wastewaters such as Zn, Cu, Fe, Mn, Co and Ni as hydroxides [18]. However, the main drawback of this modality is that complete precipitation or reduction of metals to an acceptable level for discharge requires a large amount of chemicals [14]. Other drawbacks of precipitation are its slow metal precipitation, the large volume of sludge it can produce that requires further treatment, and the long-term environmental impacts of sludge disposal [14].

2. **Ion exchange:** this is a technology that has been employed successfully in the industry for the removal of heavy metals from an effluent [14, 18]. Ion exchange transfers one or more ionic species from a liquid phase to a solid phase using a matrix of a synthetic organic ion exchange resin [18, 24]. Ion exchangers are either anion exchangers, cation exchangers or amphoteric exchangers (exchangers that are capable of exchanging anions and cations simultaneously). The most commonly used solid cation exchange resins have either a strong sulfonic acid group ($-SO_3H$) or a carboxylic acid group ($-COOH$) [20]. This allows a reversible cation exchange between the solid and the liquid phase by replacing the H^+ from the functional group with the metal ion from solution [20]. The main disadvantage of this technique is its inability to handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater [14]. This limitation poses a major bottleneck when it comes to applying this technique to handle concentrated metal solutions. Additionally, ion exchange is highly sensitive to the pH of the solution and rather nonselective [14].
3. **Adsorption:** This is another sorption-based operation, where metal ions get entrapped by adsorbents through physical or chemical interactions [20]. Adsorbents are materials that are highly porous, have a large surface area, and active functional groups. Adsorbents commonly used in industry are mineral organic materials, activated carbon, zeolites, biomass, and natural or synthetic

polymeric materials [18, 20]. The main disadvantages of this method are the low selectivity, relatively high capital and operation costs due to the progressive deterioration of the adsorbent's capacity as the number of cycles increases [17].

- 4. Membrane filtration (pressure-driven ultrafiltration, reverse osmosis and, nanofiltration and electric field-driven electrodialysis):** This is a semi permeable phase which has the ability to restrict the motion of different species to a different extent[24]. The properties of a species govern the rate of its transfer through this barrier. This technique first emerged for metal recovery in 1970 by Bhattacharyya et al., who investigated the feasibility of using a charged ultrafiltration membrane to recover Cu, Ni and Zn ions [20]. Membrane filtration is efficient even at high concentration and only requires a small space [17]. The main disadvantages of this technique are the low throughputs, lack of selective metal recovery and the high operation costs due to membrane fouling [14, 17, 25].
- 5. Electrolytic recovery or electro-winning:** This technology is applied to recover metals from waste-water streams. It is mainly used for acid solutions saturated with metals. In this technique, electric current passes through a metal solution containing an insoluble anode and a cathode plate. The negatively charged cathodes attract the positively charged metal ions leaving behind a metal deposit that can be stripped and recovered. This process can be considered clean and environmentally attractive since the electron is the main reagent of the reduction reaction [18, 26]. However, the main limitation of this process is corrosion and electrodes have to be replaced frequently [14, 27].

The main advantages and disadvantages of the technologies mentioned above are summarised in Table 1.1. The majority of these techniques come with certain limitations such as high capital and operational costs, poor effectiveness at low metal concentrations, and the production of large amounts of sludge that needs further treatment [14, 25]. Traditionally, liquid-liquid extraction (LLX) is one of the most widely used hydrometallurgical techniques for metal separation and recovery, as both capital and operational costs are relatively low [28-30]. Furthermore, LLX employs relatively simple equipment and requires small quantities of reagent that can be re-generated in most of the cases [31].

Table 1.1: Summary of the main advantages and disadvantages of conventional technologies used for heavy metal recovery from process streams [14, 18, 20].

Treatment method	Advantages	Disadvantages
Chemical precipitation	<ul style="list-style-type: none"> • Low capital cost • Simple operation • High degree of selectivity 	<ul style="list-style-type: none"> • Ineffective to treat concentrated heavy metal solutions • Needs large amount of precipitants • Generation of toxic sludge • Extra operational cost for sludge disposal • Incomplete removal • Time consuming process
Ion exchange	<ul style="list-style-type: none"> • Fast kinetic • High regenerability of resin materials • Relatively cheap 	<ul style="list-style-type: none"> • Nonselective • Highly sensitive to the solution pH • Can't handle concentrated solutions as the matrix gets easily fouled • Regeneration of resin is required
Adsorption	<ul style="list-style-type: none"> • Modest operating conditions • Relatively cheap • Wide range of adsorbents 	<ul style="list-style-type: none"> • Low selectivity • Complicated post treatment process • Waste production • No regeneration of the sorbent
Membrane filtration	<ul style="list-style-type: none"> • Small space requirement • Low pressure • High separation efficiency for single metal 	<ul style="list-style-type: none"> • High capital cost • High operational cost due to membrane fouling and energy consumption • Low flow rates
Electrolytic recovery or electro-winning	<ul style="list-style-type: none"> • Environmentally attractive 	<ul style="list-style-type: none"> • Electrodes corrosion

1.3 LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction, also known as solvent extraction, is the most commonly applied technique to separate metal ions [32]. This technique is performed by separating a solute based on its relative solubility in two different immiscible liquids that are in contact with each other [33-36]. The two phases are typically an aqueous solution (polar) and a water-immiscible organic solvent (non-polar) [37]. The distribution coefficient (D) or the partition coefficient (m) is a thermodynamic measure for the distribution of the solute between the two immiscible solvents and is defined as the ratio of concentrations of a solute in the organic phase (extract) C_{org} and aqueous phase (raffinate) C_{aq} at equilibrium:

$$D = \frac{(C_{org})_{Total}}{(C_{aq})_{Total}} \quad (1.2)$$

$$m = \frac{(C_{org})_{free}}{(C_{aq})_{free}} \quad (1.3)$$

The distribution coefficient refers to the equilibrium concentration ratio of all species of the solute (i.e., free and complexed), whereas the partition coefficient refers to the equilibrium concentration ratio of a single species of the solute e.g., only its free form [38]. In industrial applications, the term extraction efficiency (η_E) is commonly used. The extraction efficiency is defined as the percentage of the total amount of solute that is removed from the aqueous solution, calculated and expressed as:

$$\eta_E = \frac{(C_{org})_{Total} V_{org}}{(C_{org})_{Total} V_{org} + C_{aq} V_{aq}} \times 100\% \quad (1.4)$$

The propensity of a solute, in particular metal ions, to distribute between the two phases depends not only on its own properties but also on the physicochemical properties and compositions of both liquid phases [39]. Additionally, these properties determine whether the metal is extracted as a metal cation M^{n+} , as a metalate anion MX_x^{n-} , or as a neutral metal salt MX_n [40]. The difference in the physicochemical properties between the aqueous and organic phase involved in the LLX leads to a substantial difference in their behaviour. Under normal conditions, water is a liquid because the mutual interaction between the strongly polarized water molecules compensates for the negative entropic effect of ordering the structure of liquid water [39]. The ordered water structure is a result of the same electrostatic interaction between its molecules. On the other hand, the entropic effect in organic solvents, where weak Van der Waals force interactions prevail, makes their liquid structures disordered [39]. The properties and composition of both phases can be easily adjusted in the experiment which makes LLX so flexible and versatile when it

comes to metal ions separation [39]. For instance, changing the pH of the aqueous phase or adding salting out agent leads to substantial differences in the distribution of the solute between the two phases.

In LLX processes, mass transfer between two liquid phases can be accompanied by a chemical reaction (such as complexation reaction). Even a mere physical partitioning of a neutral molecule is accompanied by a chemical change in the solvation environment of the partitioned molecule [33]. The overall kinetics of the LLX process depends on both the transport rates between the two phases and the rates of the chemical reactions [39]. The rate of the overall process is controlled by the slowest step, be that a transport step or the kinetics of the any of the chemical reactions involved. In general, using extractants that complex with the metal ions adds extra complexity to the analysis. One reason is that the reaction can occur not only within the bulk of either phases but also at the interface [33]. For example, if the extracted metal complex formed at the interface, one should also consider the effects of diffusion of the reactants from the bulk of both phases to the interface and the diffusion of the product (i.e., the metal complex) from the interface to the bulk of the extractant.

LLX is a multi-step operation that consists of a first step in which the targeted metal ions are temporarily transferred into a solvent and a second step in which the metal ions are separated from the loaded solvent to allow further processing. High affinity of the metal ion toward the applied solvent is ideal for the first step, however a proper regeneration ability of the loaded solvent is crucial for the second step. After contacting and subsequent separation of the two liquid phases in the first step, the solvent needs to be unloaded and regenerated. This means that a proper optimization of the second step is a key factor in determining the success of any potential LLX process [10]. Therefore, maintaining the right balance between the required high affinity in the first step and demanded reversibility in the second step is crucial. Moreover, the phase separation involved in both steps should be taken into consideration as well which requires a careful evaluation of the hydrodynamic behaviour and operational mode. For example, vigorous mixing might be favourable to enhance mass transfer and accordingly metal extraction or regeneration, nevertheless it may lead to a more difficult phase separation due to emulsion formation [41].

It is generally acknowledged that popularity of LLX process relies mainly on the ease of adjusting its main controlling parameters such as the pH of the aqueous solution, the nature of the extractant and the diluent or the compositions of both liquid phase [32]. However, the use of large volumes of volatile organic solvents (VOCs), such as gasoline, benzene, formaldehyde, toluene, chloroform and tetrachloroethylenes, is of great environmental concern [10, 30]. Especially because not only the volatility, toxicity and/or flammability of these VOCs are an issue, but also their negative impact on human health once their vapor

is emitted into the air [32]. Therefore, there is a serious need for more environmentally friendly solvents to replace the ones currently applied in industrial processes. In recent years, ionic liquids (ILs) have been investigated intensively for metal extraction processes as they have been shown to possess certain characteristics that appear superior to those of conventional VOCs such as its low volatility, low flammability and tuning ability [42, 43].

1.3.1 IONIC LIQUIDS

ILs were discovered in 1914 by Paul Walden who, during his search for molten salts, found that ethyl-ammonium nitrate has a melting point of 12°C. The implication of his finding was that he could run his experiments studying these molten salts at room temperature [44, 45]. ILs are defined as molten salts that are composed of an organic cation and an organic or inorganic anion, and are generally liquid below 100 °C [10, 32, 46, 47]. The most widely investigated ILs, categorized along their cation, are ammonium, imidazolium, phosphonium, pyridinium and pyrrolidinium-based ILs [32, 46, 48]. They have unique physicochemical properties such as very low vapor pressure, non-flammability, high thermal stability, good solvation ability and display a wide liquidus temperature range [42, 43]. Different ions can be incorporated in ILs and it is possible to change the existing cations and anions to create new and different ILs, with the number of different combinations essentially infinite. This possibility makes ILs to be recognized as “designer solvents” and a proper selection of ions is essential to develop an environmentally acceptable IL with the desired properties for a specific task such as an extractant in (metal) extraction. Most importantly, ILs exhibit higher metal distribution coefficients at very low raffinate concentrations and are ideal for treating dilute aqueous streams [49].

1.3.1.1 ARE IONIC LIQUIDS GREEN SOLVENTS?

As already reported in the literature, ILs exhibit high thermal stability and cause insignificant air pollution compared to VOCs due to their extremely low vapor pressure [50-52]. In addition, the toxicity of IL's towards mammals is rather low [50-52]. However, the principle of green chemistry requires that a multidimensional risk analysis is carried out in order to assess the environmental sustainability of ILs [53]. Therefore, the aforementioned properties of ILs are not sufficient to classify ILs as a “green solvent” due to their solubility in aqueous media, as this may lead to water pollution and threaten the aquatic environment. In general, the effect of anions on the toxicity and biodegradability is secondary compared to the effect of the cations, but their broad diversity did not allow a conclusive analysis [54, 55]. Regarding the cationic counterpart, pyridinium based ILs have been found to be less toxic and more biodegradable than imidazolium and phosphonium ILs [53, 56]. Additionally, it is reported that introducing a functional polar group, such as an oxygen atom, to the alkyl chain decreases the toxicity of ILs and increases the biodegradation efficiency to some extent [54, 55, 57]. This indicates the possibility of tailoring ILs by coupling suitable functional groups to their structure, which in turn leads

to a more environmentally friendly compound. On the other hand, it was observed that an increase in alkyl-chain length, and with that increase their hydrophobicity, increases both the toxicity as well as the rate of degradation [55]. This highlights the effect of a single parameter on two conflicting interests, on the one hand, minimizing the toxicity, on the other hand, maximizing the biodegradability of these solvents.

In future, to move beyond the toxicity and/or low biodegradability rate of ILs toward (new) potential applications, there are two possible paths that can be considered based on the limited available ecotoxicological evaluation of ILs [54]:

1. The development of innovative ILs, which are green and safer, and their application in environmentally friendly processes such as the use of Cholinium hexanoate in the extraction of suberin from cork where it plays the dual roles of solvent and mild catalyst [58].
2. The exploration of ILs in biological applications, such as the replacement of the highly volatile and toxic formalin by 1-alkoxymethyl-3-methylimidazolium tetrafluoroborate in embalming, tissue preservation and as wood preservative where their unique toxic (antimicrobial) properties become advantageous [59-62].

Nevertheless, due to the wide variety of different ILs available, one should be careful when generalizing their properties. Comprehensive studies are needed to examine each IL separately before conclusions are drawn.

1.3.1.2 INDUSTRIAL APPLICATIONS OF IONIC LIQUIDS

Since their discovery, ILs have been investigated for a wide range of applications in chemistry, engineering and material science. This is mainly due to the physicochemical properties of an IL which can be tuned for specific applications. This has led to tremendous research efforts over the past two decades, publishing thousands of papers in many fields, filing numerous patents and commercializing new products and processes that utilize ILs (Figure 1.4) [63]. Despite the relatively high price of ILs, they are still attractive to investors and companies since they have been proven to be competitive within capital expense (CAPEX) and operating expense (OPEX) budgets [63].

Figure 1.4: The number of publications and patents per year from 1990 to 2020, obtained using the SciFinder™ database containing the keyword “ionic liquid”.

In 2002, BASF in Germany announced the first time use of an IL at a commercial scale where it serves as an auxiliary in BASIL™ process. In this process ILs are used as acid-scavenging agents during the production of alkoxyphenylphosphines in order to avoid solid formation resulting from the use of conventional triethylamine [63]. ILs have also been used as performance additives in a number of industries, such as 3M who developed ILs as antistatic additives to improve safety (reduce electrostatic discharge) and cleanliness (reduce particles and dust) [64]. Another successful example is the commercialisation of a “Natural Fibre Welding®” process in which the IL $[C_2mim][AcO]$ is used to process natural fibres (cellulose, hemicellulose, silk, etc.) to establish a congealed network that maintains the native polymer structure [65]. For a broader overview about the commercial applications of ILs, the reader is referred to the relevant literature [63, 64, 66].

However, while using ILs as a solvent for metal extraction has received great interest in the literature, only a limited number of processes are known to have been piloted. To the best of our knowledge, Seren Technologies is the only pre-commercialized process which applies ILs to extract and separate a mixture of rare earth metals (i.e., dysprosium and neodymium) found in spent permanent magnets used in electric vehicles [67, 68]. The main advantages of this technology are 1) high selectivity (i.e., 98%) in a single separation step, 2) time-saving (only two hours), 3) low acid consumption (operate at pH between 2 and 4), 4) IL is fully recyclable and 4) applying another IL as a diluent instead of VOCs [68]. The piloting and commercialization of ILs are still missing in the extraction processes of transition metals (e.g. Co) despite the increasing demand and supply problems resulting from the fast-growing market of electric vehicles. Therefore, it is important for researchers,

inventors and investors to focus on upscaling, piloting and commercialising ILs for this goal instead of quitting at on batch level after filling patents. Even though it is argued that ILs are not innately green, they still can improve the green matrix of a process by making it more sustainable through increased recyclability of the used IL.

1.3.2 INDUSTRIAL LIQUID-LIQUID EXTRACTORS

Extractors are classified based on the way of dispersing the phases and the counter current flow pattern that they create. Phase contact is achieved using either gravitational force or centrifugal force. Table 1.2 summarizes the main advantages, disadvantages and industrial applications of the main commercially available extractors.

1. **Mixer-settlers:** one of the simpler extractors, mixer-settlers function in two stages. The first stage involves mixing the two liquids phases in a vessel to accomplish mass transfer and the second stage separates and settles the phases naturally by gravity as shown in Figure 1.5 [24]. One of the liquid phases is dispersed as small droplets into the other liquid, and allowing the necessary agitation and residence time, the performance reasonably approaches equilibrium. These units can be connected together in series to realize a multistage counter-current cascade. It is widely used in the chemical industry and especially in petrochemical, nuclear, fertilizer and metallurgical processes [69].

Figure 1.5: Mixing vessel with turbine agitators [69].

2. **Mechanically agitated columns:** these columns employ a different type of mechanical devices to agitate the liquids as they pass through the column to enhance mass transfer via increasing the interfacial area. Rotating and reciprocating mechanisms are the most popular techniques for creating and maintaining dispersion throughout the column. The most commonly used rotary agitated extractors are the Scheibel column, Rotating-disk contactor (RDC), Asymmetric rotating-disk (ARD) contactor, Oldshue-Rushton multiple mixer column and Kuhni column (Figure 1.6) [69]. The specification of these columns makes them useful for when the interfacial tension is high, the density

difference between the two phases is low as well as when the liquid viscosities are high [70]. This is because relying exclusively on gravitational forces under the aforementioned conditions is insufficient for proper phase dispersion and turbulence [70]. Furthermore, reciprocating plate columns such as KARR can perform phase dispersion in a more efficient way. This is because they require less energy. Yet are still able to provide the same effect of other rotary agitated columns in terms of mixing patterns and uniform dispersion [24]. These columns are suitable for processing corrosive systems, liquids containing suspended solids and mixtures with emulsifying tendencies [69, 70].

Figure 1.6: Mechanically agitated columns: (a) Scheibel column, (b) Rotating-disk contactor, (c) Asymmetric rotating-disk contactor, (d) Oldshue-Rushton multiple mixer column, (e) Kuhni column, and (f) KARR reciprocating plate column [69].

3. **Unagitated and pulsed columns:** the overall efficiency of unagitated columns, is usually quite low when compared with agitated contactors. This is due to the poor contact between the phases and the excessive backmixing in the continuous phase [24, 69]. However, these columns are still commonly encountered in industry due to their simplicity and low cost especially for processes requiring a few theoretical stages. They are also useful in corrosive systems where the absence of mechanically agitating part is beneficial. Spray column, packed column and perforated-plate column are the best known commercially available unagitated columns (Figure 1.7) [69]. To improve the efficiency of these columns, the content of the column can be exposed to sinusoidal pulsation, creating a well-distributed turbulence, enhancing mass transfer and reducing back mixing [24].

Figure 1.7: Unagitated columns: **(a)** spray column, **(b)** packed column and **(c)** perforated-plate column [69].

4. **Centrifugal extractors:** this type of extractors works through the application of centrifugal forces to perform phase dispersion. Centrifugal forces are superior to gravitational forces to accelerate phase separation and reduce contact time [24, 69]. Therefore, they are particularly useful for systems that require long time to settle, chemically unstable systems where a short contact time is desirable and systems which have a high emulsifying tendency.

Table 1.2: The main advantages, disadvantages and industrial application of commonly used commercial extractor [24, 69, 71-73].

Type of extractors	Advantages	Disadvantages	Industrial application
Mixer-settlers	<ul style="list-style-type: none"> • Good flexibility • High capacity and stage efficiency • Reliable scale-up • Handles liquids with high viscosity and wide solvent ratios 	<ul style="list-style-type: none"> • High capital cost per stage • Large footprint • Large inventory of material in the vessels 	<ul style="list-style-type: none"> • Petrochemical • Nuclear • Fertilizer • Metallurgical
Rotary agitation columns	<ul style="list-style-type: none"> • Reasonable capacity, HETS and construction cost • Many stages possible • Low operating and maintenance cost 	<ul style="list-style-type: none"> • Repair of internal mechanical parts can cause process delays • Required more time to reach steady state compared to centrifugal contactors[73] 	<ul style="list-style-type: none"> • Petrochemical • Pharmaceutical • Fertilizer • Metallurgical
Reciprocating-plate columns	<ul style="list-style-type: none"> • High throughput • low HETS • Simplicity and flexibility in construction • Handles corrosive systems • Handles liquids containing suspended solids and mixtures with emulsifying tendencies 	-	<ul style="list-style-type: none"> • Petrochemical • Pharmaceutical • Chemical • Metallurgical • Wastewater treatment
Unagitated columns	<ul style="list-style-type: none"> • Low capital, operating and maintenance cost • Simplicity in construction, • Handles corrosive material 	<ul style="list-style-type: none"> • Low efficiency • Poor phase dispersion • Excessive back-mixing in the continuous phase • Provide no more than 1-2 theoretical stages 	<ul style="list-style-type: none"> • Pharmaceutical • Chemical
Pulsed columns	<ul style="list-style-type: none"> • Quite versatile • Low HETS • No internal moving parts • Many stages possible 	<ul style="list-style-type: none"> • Poor at handling large flowrates • More expensive than agitating column 	<ul style="list-style-type: none"> • Petrochemical • Nuclear • Metallurgical

Centrifugal
extractor

- Short contact time for unstable material
- Requires limited space
- Easily handles emulsified systems and liquid with small density difference
- Complexity in construction
- High capital and operating cost
- Great maintenance requirement
- Petrochemical
- Pharmaceutical
- Chemical

* HETS is height of an equivalent theoretical stage

1.4 THESIS SCOPE AND OUTLINE

Despite the publication of numerous successful IL-based extraction studies at batch-scale, the knowledge of upscaling these processes is still very limited. This thesis aims to consider several aspects of upscaling. For this purpose, the fatty-acid-based IL tetraoctylphosphonium oleate [P_{8888}][Oleate] was chosen. The reason to take this particular IL is that [P_{8888}][Oleate] has a unique selectivity towards transition metals, which makes it a good candidate for the extraction of Co from industrial wastewater and spent synthetic LIB leachate [10, 25, 74]. This thesis is divided into multiple studies that each investigate a certain aspect of the LLX process of metal retrieval using IL. The following section summarizes the focus of each study and how they relate to the main thesis.

CHAPTER 2: IONIC LIQUID-BASED PROCESS DEVELOPMENT FOR COBALT RECOVERY FROM AQUEOUS STREAMS

In this chapter, LLX process has been investigated on batch-scale to recover Co from a chloride aqueous medium. Extraction-regeneration processes were followed during five consecutive cycles using [P_{8888}][Oleate] as the solvent and Na_2CO_3 as regeneration solution. The main focus of this chapter was to define the main criteria to judge the viability of any potential application of ILs including the extraction efficiency, the recovery and the loss of the IL and the end-product.

CHAPTER 3: RECOVERY OF METALS FROM SPENT LITHIUM-ION BATTERIES USING IONIC LIQUID [P_{8888}][OLEATE]

This chapter provides an approach to selectively extract and recover valuable metals (Co, Ni, Mn and Li) from synthetic spent lithium-ion battery cathodes leachate using [P_{8888}][oleate]. The investigated parameters for this selective separation and recovery process are the extraction pH, contact time, composition of the regeneration solution and number of required extraction/regeneration stages within one cycle. Additionally, an economic potential analysis EP0 has been performed to evaluate the feasibility of the proposed process.

CHAPTER 4: THERMODYNAMICS AND PHYSICAL PROPERTIES OF AN IONIC LIQUID-BASED METAL EXTRACTION PROCESS

This chapter presents a systematic approach to investigate the extraction mechanism of transition and alkali metal ions/salts from aqueous phase using IL [P_{8888}][Oleate]. This approach involves studying the extraction isotherm, evaluating the thermodynamic parameters (equilibrium constant, Gibbs free energy, enthalpy and entropy of metal-IL complexation reaction), as well as understanding the complexation reaction taking place between the extracted metal ions/salts and IL. This is followed by a discussion of how

the extraction process is influenced by the nature of the accompanying anion and the addition of salting out agents.

CHAPTER 5: KINETIC ANALYSIS OF AN IONIC LIQUID-BASED METAL EXTRACTION PROCESS

In this chapter, Co extraction from an aqueous stream using $[P_{888}][Oleate]$ has been performed in a single droplet extraction column. The main purpose was to investigate the mass transfer behaviour of Co extraction into IL droplet and to identify the mass transfer limitation. This has been achieved based on intensive experimental and mass transfer modelling analysis. Mass transfer with and without a chemical reaction models are evaluated using a statistical cross-validation method in which the outcome involves the effect of the following parameters: column lengths, droplet diameter, droplet rising velocity and continuous and dispersed phase concentrations on Co uptake.

CHAPTER 6: COBALT EXTRACTION IN A BENCH SCALE RECIPROCATING PLATE COLUMN

In this chapter, Co extraction from an aqueous stream using $[P_{888}][Oleate]$ has been performed in a laboratory scale reciprocating plate extraction column (i.e., 5/8" diameter KARR[®]). The focus was to assess the influence of different operating variables on the column performance including the frequency of agitation and the flow rates of the solvent and aqueous phase. Moreover, experiments were performed to study the extent to which the solvent to feed ratio affects the hydrodynamic performance of the unit without causing flooding. Additionally, a mathematical model including literature correlations for mass transfer, holdup and droplet diameter was developed. The results from this model were compared to the experimental data obtained in this study as well as those found in literature.

CHAPTER 7: CONCLUSIONS AND OUTLOOK

The last chapter of this thesis presents a bird's eye view of this project where the main results of each chapter are summarized and the main conclusions are highlighted. An outlook is presented as well to assist with continuing research on this topic.

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CHAPTER 2

IONIC LIQUID-BASED PROCESS DEVELOPMENT FOR COBALT RECOVERY FROM AQUEOUS STREAMS

If you can't explain it simply, you don't understand it well enough

Albert Einstein

ABSTRACT

Using the ionic liquid $[P_{888}][Oleate]$, liquid-liquid extraction has been studied to recover Co from synthesized wastewater. Extraction-regeneration experiments were followed during five consecutive cycles with $Na_2CO_3(aq)$ as regeneration solution. Over 99% of Co was extracted and using 0.7-1 M $Na_2CO_3(aq)$ the extracted Co was recovered for 99 % in the form of $CoCO_3(s)$. Co transfer shifted from ion-pair extraction in the first cycle to ion-exchange in the successive cycles. Thus, the measurement of a single extraction-regeneration cycle is not sufficient to perceive conclusive information about the steady-state conditions of the process. In the context of the feasibility of the technology, four key aspects are addressed: extraction efficiency, recovery of the IL, loss of the IL, and the end product.

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2.1 INTRODUCTION

Heavy metal pollution has become a serious environmental threat [1, 2]. Arsenic, cobalt, copper, lead, nickel and zinc are all pollutants that are toxic in nature and can be carcinogenic upon their accumulation in living organisms [2]. Industrial wastewater treatment aims to remove these metals and reduce the level of pollution. Additionally, the process of treatment also allows recovering these metals from waste streams. Refining the process of reclaiming metals from waste water plays an important role in establishing a functioning circular economy, especially in the current context of diminishing metal reserves worldwide [3]. As an example, this study focusses on cobalt, a metal involved in many industrial applications, ranging from aircraft engines, rechargeable batteries, paints, coatings and catalysts. The annual growth in cobalt demand is expected to increase by more than 6% in 2020 [3]. Apart from the industrial need for cobalt, from the experimental point of view, the reason to use cobalt in the present study is its distinctive sharp colour in both the aqueous and the organic phase. Its distinct colour makes it possible to observe the transfer of cobalt from one phase to the other during the extraction and regeneration phase.

In this study Liquid-liquid extraction (LLX) is used to selectively extract Co using ionic liquid (IL) as a solvent. Despite the high extraction efficiency of many ILs, their high cost hamper if not prevent their implementation in large-scale industrial applications [4-6]. To our opinion, the viability of any potential application of ILs for Co recovery (and for that matter the recovery of any other metal as well) should rely on four mandatory criteria: (1) high extraction efficiency, (2) the use of a cheap regeneration agent / method that ensures the full regeneration of the IL, also implying (3) no loss of IL, and (4) obtaining a commercially interesting Co product.

Even though the use of IL's for metal recovery has been reported previously, to the best of our knowledge the present study is the first one in addressing the combination of all above-mentioned aspects. As illustration, Table 2.1 lists published studies with some of the aspects categorized. In fact, with almost no identified metal product, Table 2.1 reflects the common practice that the design of the process starts with the extraction part and the recovery of the IL, instead of defining the regeneration product. We consider the latter approach to be the better option. Therefore, we started out with identifying $\text{CoCO}_3(\text{s})$ as valuable product and accordingly designed the process in backward direction. Figure 2.1 schematically outlines the proposed process. In the extraction step, Co is taken up by the IL and in the regeneration (IL recovery) it is back extracted from the IL and simultaneously precipitated as $\text{CoCO}_3(\text{s})$. The labeling of the streams in Figure 2.1 are used throughout the entire chapter.

Figure 2.1: Conceptual outline of the process discussed in the present study.

The majority of previous studies show that strong acids and strong bases are able to remove a wide variety of metal ions from a loaded IL [7-19]. However, the main drawback of these regeneration solutions is that they do not allow direct re-use of the IL because strong acids protonate ILs and strong bases form emulsions [7]. In the context of the above mentioned four process criteria, strong acids and bases are often used to merely investigate the extraction process on a lab-scale without considering the consequences for the overall process.

For this study, $[P_{888}][Oleate]$ was selected for Co extraction because it 1) consists of a natural hydrophobic anion and a hydrophobic cation which is assumed to minimize the losses to the aqueous phases, 2) has the ability to selectively extract transition, rare earth, alkaline earth and alkaline metals depending on the pH and composition of the feed [7], and 3) has a relatively low viscosity at room temperature (183 mPa.s) thus eliminating either the need of a hydrophobic solvent to dilute the IL [20, 21] and the need for high(er) temperatures during operation.

In earlier studies, using phosphonium and ammonium-based ILs with the same functionalized anion oleate, sodium oxalate was used as a regeneration solution in both cyclic and continuous experiments. The regeneration efficiency was below 25% in the cyclic experiments (5 cycles) and below 80% in continuous mode (180 minutes) [7, 22]. Huang et al., also used sodium oxalate for the regeneration of their acid-base coupling bifunctional IL, applied for rare earth element separation [23]. Even though the metal regeneration efficiency was higher than in the studies of Parmentier et al., [7] it took at least two days to reach a regeneration efficiency of 90-100% [23]. In the present contribution, Na_2CO_3 has been used instead of sodium oxalate as it is more environmentally friendly, more than ten times cheaper and results directly in the formation of a marketable product (i.e., $CoCO_3(s)$), which is mainly used as a catalyst and in ceramic pigments. In contrast, cobalt oxalate needs to be calcined to cobalt oxide first before it becomes a commercially attractive product suitable for industrial applications. This calcination process requires

high temperatures and produces large amounts of greenhouse gasses, notably CO_2 . In case cobalt oxide is the desired end product, calcining CoCO_3 produces half the amount of CO_2 compared to oxalate. The aim of this study was to extract and recover cobalt from industrial wastewater. Extraction-regeneration experiments were followed during five consecutive cycles using $[\text{P}_{8888}][\text{Oleate}]$ for extraction and $\text{Na}_2\text{CO}_3(\text{aq})$ for regeneration. Further, this study will help understand the extraction mechanism of the recovery process. To the best of our knowledge the aforementioned combination of tetra(octyl)phosphonium oleate and sodium carbonate as a regeneration solution producing solid CoCO_3 has not been reported at present. In order to define the steady-state conditions, the system was investigated by running five subsequent extraction-regeneration cycles.

Table 2.1: Overview of publications on metal extraction using ionic liquids.

Ionic Liquid	Metal Ions	Regeneration Solution	Recovery IL	Loss of IL in Raffinate**	Identified End Product	Extraction Mechanism	Ref
[Bmim]-[Cl]	Ce ³⁺ , Eu ³⁺ , Y ³⁺	0.05 M HNO ₃	Yes	NDA*	NDA	Cation exchange $M^{3+} \leftrightarrow 3 [Bmim]^+$	[8]
		7.0 g/L acetohydroxamic acid+ 1.0 M guanidine carbonate					
		0.05 M diethylenetriamine pentaacetic acid + 1.0 M guanidine carbonate					
Cyphos® IL 101	Co ²⁺ , Ni ²⁺	0.05 ethylenediamine tetraacetic acid + 1.0 M guanidine carbonate	Yes	40-80 ppm of [P*]	NDA	Anion exchange $MCl_4 \leftrightarrow 2[Cl^-]$	[9]
		0.1 M citric acid + 0.4 formic acid + 0.4 M hydrazine hydrate					
		500 mM [Bmim][Cl]					
CTMA TMA	Cd ²⁺ , Cu ²⁺ , Pb ²⁺	Mixture of acetone and ethylic alcohol	Yes	2 wt. %**	NDA	Anion exchange $3M^{2+}+2Y^- \leftrightarrow 2[H^+]$	[10]
[P ₄₄₄₁₄][Cl]-NaCl-H ₂ O	Co ²⁺ , Ni ²⁺	NDA	NDA	<0.2 wt. %	NDA	Anion exchange $MCl_4 \leftrightarrow 2[Cl^-]$	[11]
[P ₆₆₆₁₄][Cl]	Co ²⁺ , Ni ²⁺	5 steps stripping: 1 x 6 M HCl, 3 x pure water and, 1 x ammonia	Yes	NDA	NDA	Dissolution of metal oxides	[12]
[C ₄ mim][Tf ₂ N]	Co ²⁺ , Ni ²⁺	Nitric and sulfuric acid solution	Yes	1.40 wt. %	NDA	NDA	[13]
[Hbet][Tf ₂ N]	Co ²⁺ , Ni ²⁺	Hydrogen bis(trifluoromethylsulfonyl)imide HCl	Yes	NDA	NDA	NDA	[16]
[N ₁₈₈₈][C ₄ SAC]	Co ²⁺ , Ni ²⁺	HNO ₃ HCl	Yes	0.3-1.2 wt. %	NDA	NDA	[14]
[N ₁₈₈₈][C ₆ SAC]							
[N ₁₈₈₈][C ₆ SAC]							
[P ₁₈₈₈][C ₄ SAC]	Co ²⁺ , Ni ²⁺	1 M HCl 1 M HNO ₃ 1 M HClO ₄ 1 M Na ₂ CO ₃ 0.05 M thiourea + 0.1 M HCl	Yes	NDA	Yes, solution of metal thiourea	NDA	[18]
[P ₁₈₈₈][C ₅ SAC]							
[P ₁₈₈₈][C ₆ SAC]							
[P ₁₈₈₈][BnSAC]							
Aliquat-336	Co ²⁺ , Ni ²⁺		Yes	NDA	Yes, solution of metal thiourea	NDA	[18]

[C ₆ mim][DEHP]	Co ²⁺ , Ni ²⁺	HNO ₃	Yes	NDA	NDA	Ion exchange Nd ³⁺ $\leftrightarrow$ 3[H ⁺]	[15]
[C ₆ mpyr][DEHP]							
[N ₄₄₄₄][DEHP]							
[A336][NO ₃]	Co ²⁺ , Ni ²⁺	Milli-Q water	Yes	NDA	NDA	Hydrated anionic complex	[17]
C ₄ mimNTf ₂	Co ²⁺ , Ni ²⁺	HNO ₃	Yes	NDA	NDA	NDA	[19]

* NDA= No Data available

** Ref (22) shows weight loss percentage of the applied amount of IL's during extraction while others indicate the weight percentage of IL present in the aqueous phase.

2.2 EXPERIMENTAL

2.2.1 CHEMICALS AND REAGENTS

All the chemicals utilized in this project were of analytical grade and used as purchased. These chemicals are tetra(octyl)phosphonium bromide (>95%, Iolitec), oleic acid (90%, rest polyunsaturates <7%, unsaponifiable <0.2% and water <0.05%, Alfa Aesar), cobalt (II) chloride hexahydrate (99%, Sigma-Aldrich), sodium hydroxide ($\geq 97\%$, VWR), sodium chloride (100%, VWR), calcium chloride (Across Organics), and sodium carbonate anhydrous (100%, VWR). Throughout the synthesis, extraction and regeneration experiments, Milli Q-water (≥ 18.2 M cm) was used.

2.2.2 IONIC LIQUID SYNTHESIS PROCEDURE

Tetraoctylphosphonium oleate was synthesized according to the procedure previously reported, albeit with some modifications [22]. At first, 0.319 mol (12.74 g) of NaOH was dissolved in 800 ml Milli-Q water before adding 0.231 mol (65.24 g) oleic acid. Then the mixture was stirred (650 rpm) at 45 °C for 3 hours. After that, 0.177 mol (100 g) of $[P_{8888}][Br]$ was added to the mixture to be stirred for 8 h at 75 °C. Following Parmentier et al [9], an excess of oleic acid was applied to shift the equilibrium towards IL formation. The IL was washed nine times with, in total, 9 L of Milli Q-water using a separatory funnel in order to remove the impurities such as bromide and sodium. Finally, a rotary evaporator (BUNCHI Rotavapor®R-3) and a vacuum oven at 50 °C were used to remove the remaining amount of water. Figure 2.2 summarizes the synthesis of $[P_{8888}][Oleate]$. The water content of the IL was determined using a 756 Karl Fischer Coulometer. NMR spectra of the synthesized product identified pure $[P_{8888}][Oleate]$ IL possessing an excess of 20% oleate (results not shown), all in line with Parmentier et al. [22].

Figure 2.2: Schematic representation of the synthesis of the IL $[P_{8888}][Oleate]$.

2.2.3 ANALYSIS OF IONS AND IL CONCENTRATIONS

The concentrations of the metal cations in the aqueous phases (raffinates of extraction and regeneration) and lean IL were determined with Induced Coupled Plasma (ICP) of Perkin Elmer, equipped with an Optima 5300 DV optical atom emission spectrometer (OES). Anion and sodium concentrations were measured using a Metrohm 761 Compact ion chromatograph (IC). In order to analyse the metal concentration of the IL, prior to the use of ICP, microwave-assisted peroxide (H_2O_2) digestion of the IL was performed using the Ethos Easy advanced microwave digestion system. To that end, 0.25 g IL was added to 10 ml H_2O_2 (30%), whereupon the digestion tube was sealed and heated up to 180 °C for 220 minutes. Afterwards, before analysis the samples were cooled to a temperature between 25 and 30 °C. To determine the loss of IL to the aqueous phase the P-content and organic C-content of the raffinate were measured using ICP and Total Organic Carbon Analyzer TOC. The CoCO_3 deposit was analysed using Raman Spectrometry (Horiba Jobin Yvon LabRAM HR Raman spectrometer), Scanning electron microscopy (SEM) and energy dispersion X-ray (EDX).

2.2.4 EXPERIMENTAL PROCEDURE

Feed solutions were prepared with a concentration of 1 g/L of Co and Na from their corresponding Cl salts unless otherwise stated. For the first extraction cycle, 5 ml of this solution was added to 5 ml of water-saturated [P_{8888}][Oleate] (water content around 10 wt.%) and mixed at room temperature for 2 hours using a Heidolph Multi Reax vortex mixer at a speed of 2500 rpm. For the first three cycles the volume ratio was unity while for the fourth and the fifth cycle the ratio changed because the volume of the IL decreased to less than 2.5 ml due to sample-taking for analysis. Table 2.A.1 shows the volumes of feed ($V_{f,i}$), regeneration solutions ($V_{Rf,i}$) and IL (V_{IL}) used in the subsequent cycles. In order to account for the variable volume ratio during consecutive cycles, all ion concentration calculations have been corrected (normalized) by multiplying the measured Co concentration in the IL phase by V_{IL}/V_{aq} (see Appendix 2.A for details). This is possible since in all cases almost full extraction (>99%) of the Co was obtained. Therefore, a lower V_{IL}/V_{aq} ratio would not lower the extraction efficiency. Prior to the experiments described here, a separate test applying different contact times revealed that 2 hours are more than sufficient to reach equilibrium (actually, more recent tests showed that even 10 minutes would have been enough). To enhance the phase separation, the mixture was then centrifuged using an Allegra X-12 R Centrifuge (Beckman Coulter) at a speed of 3750 rpm for 20 minutes.

After each extraction the hydrophobic ionic liquid (HIL) loaded with Co was regenerated using different concentrations of Na_2CO_3 (i.e., 0.3, 0.5, 0.7 and 1.0 M), following the same analytical procedures that were applied for the extraction. From that point, the (partly) regenerated IL was exposed to fresh feed solution for the next extraction cycles.

This procedure was repeated for five complete subsequent cycles of extraction and regeneration.

2.2.5 CALCULATION OF EFFICIENCIES AND PRODUCTIVITY

The aqueous solutions after extraction and regeneration as well as the lean IL were analysed for Co. The extraction efficiency (η_E) is defined as the percentage of Co that is removed from the feed, calculated and expressed for cycle i as:

$$\eta_{E,i} = \frac{(C_{f,o} - C_{r,i}) V_{f,i}}{(C_{f,o}) V_{f,i}} \times 100 \% \quad (2.1)$$

Note that this expression assumes equal volumes of feed and raffinate which is realistic since the IL is pre-saturated with water.

The regeneration efficiency (η_R) is defined as the percentage of Co that is removed from the IL, calculated and expressed for cycle i as:

$$\eta_{R,i} = \left(1 - \frac{C_{LeIL,i} V_{IL,i}}{C_{LoIL,i} V_{IL,i}} \right) \times 100\% = \left(1 - \frac{C_{LeIL,i} V_{IL,i}}{(C_{f,o} - C_{r,i}) V_{f,i} + C_{LeIL,(i-1)} V_{IL,i}} \right) \times 100\% \quad (2.2)$$

It is to be noted that for $i=1$, the value of $C_{LeIL,0}$ is zero, implying that the experiment starts with a Co-free IL.

Additionally, the denominator of the right term of expression 2.2 is comprised of two contributions, the first representing the freshly extracted Co from the feed, and the second representing the Co residing in the IL already due to the incomplete regeneration during the previous cycle(s).

The recovery of $\text{CoCO}_3(s)$ ($R_{\text{CoCO}_3(s),i}$) is defined as the percentage of the Co extracted that precipitates in the consecutive regeneration:

$$R_{\text{CoCO}_3(s),i} = \left(\frac{V_{f,i}(C_{f,o} - C_{r,i}) - V_{IL,i}(C_{LeIL,i} - C_{LeIL,(i-1)}) - V_{RF,i}C_{RR,i}}{V_{f,i}(C_{f,o} - C_{r,i})} \right) \times 100\% \quad (2.3)$$

The cumulative recovery ($R_{\text{CoCO}_3(s),j}^*$), being the amount of Co precipitated over the cycles 1 to j over the amount of Co extracted over these cycles, is given by:

$$R_{\text{CoCO}_3(s),j}^* = \sum_{i=1}^j R_{\text{CoCO}_3(s),i} \quad (2.4)$$

2.3 RESULTS AND DISCUSSION

2.3.1 CO EXTRACTION AND REGENERATION EFFICIENCY AND RECOVERY

Sodium chloride was added to all feed solutions because it enhances Co extraction. Even though the extraction without NaCl in the feed is already as high as 91%, adding NaCl further improves the efficiency to 99% (Figure 2.3).

Figure 2.3: Co extraction efficiency (η_E) using $[P_{888}][\text{Oleate}]$ in the presence and absence of NaCl.

Figure 2.4 shows the normalized Co concentration during five consecutive cycles of extraction and regeneration, using a 0.5 (A), 0.7 (B) or 1.0 M (C) Na_2CO_3 solution for regeneration. Panel D shows photographs taken after the first regeneration using different $\text{Na}_2\text{CO}_3(\text{aq})$ concentrations with the Co-containing, purple-coloured IL phase on top and the solid CoCO_3 precipitate collected at the bottom of the tubes. For comparison, the most left test tube contains pure IL. It is clearly visible from the decolorization of the upper phase that a higher $\text{Na}_2\text{CO}_3(\text{aq})$ concentration results in a higher back-extraction of Co. The composition of the formed precipitate was evaluated using Energy Dispersive X-ray fluorescence spectrometry (EDX). The main component of each composite was cobalt and oxygen with an atomic ratio of 1 to 3, confirming the hypothesis that the precipitate presents indeed CoCO_3 . The weight percentage (wt.%) of Co in the solid product is around 45%, whereas impurities (i.e., sodium and phosphorus) make out less than 1%. This weight percentage is in agreement with commercially available CoCO_3 with Co wt.% ranging from 43-47% [24]. In addition to EDX, Raman spectroscopy identified the precipitate as well as CoCO_3 . Details on the analysis of the precipitate can be found in Appendix 2.B.

Figure 2.4: Normalized Co concentrations in the IL after extraction and regeneration during 5 cycles ($C_{IL,i}$), using Na_2CO_3 solutions of either 0.5 M (A), 0.7 M (B) or 1.0 M (C). The SD of the measured Co concentration in the feed is 12 mg/L resulting in a same SD for the calculated Co concentration in the IL of 12 mg/L. Error analysis assuming an error of $2*SD = 24$ mg/L in the feed concentration and 2.5% in the volume resulted in an error of 5% in the normalized concentration, hence the 5% error bars shown in plots A-C. Panel D shows the first regeneration step at the three different carbonate concentration used.

Figures 2.5 and 2.6 show the extraction efficiency (2.5), the regeneration efficiency (2.6 A), the recovery (2.6 B) and the cumulative recovery of $CoCO_3(s)$ (2.6 C), respectively, for the different concentrations of Na_2CO_3 (and including 0.3 M $Na_2CO_3(aq)$). Independent of the cycle number and the concentration of $Na_2CO_3(aq)$ in the regeneration feed, the extraction efficiency was (nearly) 100% (see Figure 2.5). In contrast, the regeneration efficiency and the (cumulative) recovery did show a dependence on cycle number and/or the concentration of $Na_2CO_3(aq)$ in the regeneration feed (see Figure 2.6). For all $Na_2CO_3(aq)$ concentrations, the regeneration efficiency stabilized in the 5th cycle around $96 \pm 3\%$, whereas the recovery of $CoCO_3(s)$ stabilized around $99 \pm 3\%$. The cumulative recovery of $CoCO_3(s)$ after 5 cycles increased from 91 to 97% when increasing the $Na_2CO_3(aq)$ concentration from 0.3 to 1 M. The major part of the missing Co is present as based load in the lean IL and lost via the IL samples needed for the analysis of the IL phase.

Figure 2.5: Average Co extraction efficiency, $\eta_{E,i}$, of $[\text{P}_{888}]\text{[Oleate]}$ over five cycles after regeneration with 0.3 M, 0.5 M, 0.7 M and 1.0 M Na_2CO_3 solutions. Error percentage is 2 % based on error analysis. Shaded bars for the first three cycles refer to 1:1 IL without excess oleate, using 1 M Na_2CO_3 as regeneration solution (see also main text).

It was observed (see Figure 2.4 A-C) that upon increasing the $\text{Na}_2\text{CO}_3(\text{aq})$ concentration the steady state Co content of the lean (regenerated) IL reduced, e.g. from 150 mg/L to 60 mg/L after increasing $\text{Na}_2\text{CO}_3(\text{aq})$ from 0.5 to 1.0 M. The plots of the (normalized) Co concentration in the IL show that when using 1 M $\text{Na}_2\text{CO}_3(\text{aq})$ steady-state sets in earlier as compared to when using 0.5 or 0.7 M $\text{Na}_2\text{CO}_3(\text{aq})$. The same trend was observed for the regeneration efficiency and the (cumulative) recovery of $\text{CoCO}_3(\text{s})$ (see Figures 2.6 A-C). For 0.3 M $\text{Na}_2\text{CO}_3(\text{aq})$, both the regeneration efficiency and recovery were below 40% in the first cycle showing that under these conditions the IL initially accumulates a significant amount of the extracted Co. Note that the fact that the recovery percentage can exceed the 100% level (Figure 2.6 B) is implicit in its definition and a consequence of the Co remaining in the IL due to incomplete regeneration in the previous cycle. In conclusion, these results provide a proof-of-principle regarding the near 100% Co extraction efficiency from the feed, the renderability of the IL, and maintaining a high extraction efficiency during the next cycle. If using 1 M Na_2CO_3 , 97% of the Co is recovered rendering $\text{CoCO}_3(\text{s})$ as end-product. In addition, the mass balance results show that the measurement of a single extraction-regeneration cycle is not sufficient to identify the steady-state of this process as it takes 2 to 4 cycles (depending on the Na_2CO_3 concentration) to reach an operating point where accumulation effects in the IL can be neglected.

Figure 2.6: Regeneration efficiency $\eta_{R,i}$ of Co-loaded $[P_{888}][Oleate]$ (A), Co recovery $R_{CoCO_3,i}$ (B) and cumulative Co recovery $R^*_{CoCO_3,j}$ (C) using Na_2CO_3 solutions of various concentrations (0.3 – 1.0 M), during five cycles of operation. Based on error analysis, estimated errors are 3% and 5% for the regeneration efficiency $\eta_{R,i}$ and the (cumulative) recovery $R_{CoCO_3,i}$ and $R^*_{CoCO_3,j}$, respectively.

2.3.2 ION TRANSFER

The majority of previous studies concluded that the extraction of metal ions by ILs is based on a mechanism of ion exchange, a process in which the IL may participate in [8-12, 25, 26]. In order to check whether $[P_{888}][Oleate]$ demonstrates similar behaviour, the transfer of all ion species present between aqueous and organic phase was analysed. Figure 2.7 shows the absolute amounts (in μmol) of Co, Na, Cl and $[P_{888}]$ exchanged between the feed and lean IL for the first and second extraction cycles using 0.1 M $Na_2CO_3(aq)$ during the intermediate regeneration step. The 1st cycle clearly shows a nearly 1:2 molar transfer of Co and Cl from the feed to the lean IL. This observation indicates that Co extraction is through ion pair uptake, together with Cl. Importantly, based on the numbers shown in Figure 2.7 A, the charge balance, referenced to the IL phase, is -3 (μmol of elementary charge). Already during the second cycle the transfer process moved into the direction of ion exchange. Here the movement of Co out of the feed into the lean IL was accompanied

by the counter movement of Na out of the IL into the feed. At steady state, the source of this Na is the $\text{Na}_2\text{CO}_3(\text{aq})$ used for IL regeneration. As was observed for the first cycle, the charge balances for the second cycle are essentially closed as well, independent of the concentration of $\text{Na}_2\text{CO}_3(\text{aq})$ during the regeneration step in between (see Figure 2.C.1). Noteworthy, the charge balance data were based on five independent analyses, i.e., the measurement of the five individual ion species present. Increasing Na_2CO_3 concentration to 1 M leads to a faster switch of mechanism (in one cycle) as shown in Figure 2.C.1. The fact that these balances are (nearly) closed reflects, first, the reliability of these measurements and, secondly, that the possible contribution of other ion species (e.g. H^+ and OH^-) to the overall charge balance is only minor. For all cases shown in Figures 2.7 and 2.C.1 the pH of the raffinate increased from 5 to 7.9 during extraction. This is partly due to Co extraction next to H^+ transfer. A dedicated experiment showed that the pH increased from 5 to 6.2 by only Co transfer. The rest is due to H^+ transfer, which is equal to $0.003 \mu\text{mol H}^+$, an amount that is negligible compared to the total amount of all other ions transferred.

The observed shift in uptake mechanism, in turn, points to an important conclusion as well. One of the key parameters for process design is the mechanism of, in this case, Co uptake by the IL during steady state. As Figures 2.7 and 2.C.1 show, conclusive information regarding the nature of the uptake mechanism cannot be established by the analysis of merely a single cycle. This is because as long as the system has not yet reached steady state, the uptake mechanism may change. A conceptual design of the process outlined here is discussed in section 2.4.

As remarked in section 2.2.2, the presence of excess oleate during synthesis resulted in a 20% oleate excess in the finally obtained $[\text{P}_{888}][\text{Oleate}]$. To assess the possible role of this excess oleate in terms of the mechanism of Co uptake, the experiments of Figure 2.7 A were repeated but with an IL without oleate excess, i.e., containing 1:1 molar amount of $[\text{P}_{888}]$ and $[\text{Oleate}]$ and using 0.1 M Na_2CO_3 (Figure 2.7 B). Even though the absolute numbers may slightly differ, the key observation and conclusion remain the same, i.e., a shift from ion pair-like uptake during the first cycle towards an ion exchange-like uptake in the second cycle. Also, in this case, charge balances were nearly closed. The extraction efficiency of this 1:1 IL during the two cycles was above 99%, very similar to the values obtained with the IL containing excess oleate (Figure 2.5). These results justify the conclusion that the presence of 20% excess oleate in the IL does not (significantly) alter its behaviour.

Figure 2.7: Absolute amount of ion species exchanged (in μmol) between aqueous ($\text{CoCl}_2 + \text{NaCl}$) and organic IL phase during extraction, calculated for the first and second cycle. The intermediate regeneration step was performed with 0.1 M $\text{Na}_2\text{CO}_3(\text{aq})$. Panels a) and b) refer to an IL with (A) and without 20% excess oleate (B).

Figure 2.7 also shows another key feature of the system studied here, especially the properties of $[P_{8888}][\text{Oleate}]$. In the first and second cycle the amount of $[P_{8888}]$ passing to the raffinate was always below 0.3 μmol ($\approx 26 \text{ mg/L}$). Compared to the amount of transferred Co (approximately 80 μmol) this is just a very small amount. This observation is in line with TOC analysis, showing a concentration of organics (IL and/or oleate) in the raffinate in the range of 10-50 mg/L.

2.4 CONCEPTUAL PROCESS DEVELOPMENT

Conceptually, the process consists of an extraction step in which Co is taken up by the IL and a regeneration step in which it is back extracted from the IL and simultaneously precipitated by, in this case, $\text{Na}_2\text{CO}_3(\text{aq})$. The proposed process does not make much sense for a feed just containing a Co-salt, because mixing the feed with solid $\text{Na}_2\text{CO}_3(\text{s})$ would have the same result without the need of using the IL, nor extraction and regeneration devices. The only advantage of extraction - regeneration for this feed would be concentrating

the Co which may simplify its precipitation. The proposed process concept seems most applicable for:

- Extraction of a mixture of metals by a non-selective IL and the subsequent precipitation of each metal in a stepwise approach by using different regeneration salts. The advantage is the treatment of IL with the regeneration salt without mixing it with the water feed and avoiding the presence of the salt anions in the extraction raffinate (feed cleaned from Co).
- Selective recovery of metals. The IL used demonstrated selectivity between transition and (earth) alkali metals, though under extreme pH conditions and rather narrow pH windows [9]. Further research is needed to develop more selective HILs that operate under more neutral pH conditions.

Figure 2.8 schematically presents the conceptual flowsheet of a Co extraction/regeneration process combined with a stream table. The extraction column is fed at the top with wastewater containing cobalt chloride and sodium chloride. The recirculated IL enters at the bottom of the column and moves as small droplets to the top, while extracting the Co out of solution. It should be stated that this is only one of the operation modes possible, alternatives are the Karr column, Kuhni column or Rotating Disk Column (RDC). It is important for the mixing to not be vigorous to avoid emulsifying the two liquids. This last requirement makes the Karr column an interesting alternative. The Co-loaded ionic liquid, due to phase separation collected at the top of the column, is transferred to the regeneration column. Here the IL is contacted (again as small droplets moving up the column) with an aqueous sodium carbonate solution in order to perform the back-extraction of Co and the regeneration of the IL. The Co-lean IL collected at the top of the column is recycled to the extraction column. More recent analysis of the batch extraction experiments showed that a contact time of 5-10 minutes is sufficient to reach equilibrium. By adjusting the droplet size and the operation mode of the extractor, the rise velocity of the droplet can be controlled. In combination with the column height the residence (contact) time can be adjusted. As mentioned above, the LLX column should enable a contact time of at least 10 minutes. The solid CoCO_3 will settle at the bottom and leave the column with the water stream. The two-phase separator next in line to the regenerator serves to separate out the solid cobalt carbonate (end-product). In more detail, the methodology applied depends on the properties of the solid (e.g., density, particle size) and can range from a relatively simple gravity separator to a filtration unit or a centrifugal separator. Preliminary experiments showed that the solids settle easily. An effective regeneration process does not require per se the full, 100%, removal of the solids from the regeneration fluid before recycling. The separated sodium carbonate solution is pumped back to the regeneration column. In case of excess water, a purging process is carried out,

after which fresh sodium carbonate is added. It is important to note that the IL will also be loaded with some NaCl.

The data presented in the stream table are calculated based on the mol/mass balance for the different components, the distribution coefficient for Co (assumed to be minimal 5, which was confirmed with equilibrium experiments) as well as analysis data for the different ions in the system. Furthermore, it is assumed that steady-state is obtained (Co exchanged for 2 Na), no IL is lost to the water phase (which means no fresh IL needs to be added to the system) and all the water added to the regeneration cycle through the fresh soda leaves during the purge. Charge balance calculations (not added) for the IL phase revealed that not all ions present in the IL were analyzed. The mass balance calculation shows that operating with a Feed to Solvent ratio of 5 (mass based) in the extraction and the regeneration column is possible. This will reduce the flow in each recycle by a factor of 5 (see total of stream S-1, S-4 and S-6 in the stream table) and consequently the equipment size is reduced as well. Regeneration with 1 M Na_2CO_3 results in a concentration drop to 0.6 M, which is still acceptable for the regeneration efficiency.

Kg/h	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	Purge	Fresh Soda	CoCO ₃ Solid
H ₂ O	995.00	995.00	17.73	17.73	17.73	35.78	45.78	35.78	32.56	3.22		3.47
IL	0.00	0.00	179.31	179.31	179.31	0.00	0.00	0.00	0.00	0.00		
Co	1.00	0.01	0.01	1.00	0.01	0.00	0.00	0.00	0.00	0.00		
Na	1.00	1.78	1.70	0.92	1.70	1.85	1.07	1.07	0.98	0.1	0.89	
Cl	2.75	2.75	1.19	1.19	1.19	0.00	0.00	0.00	0.00	0.00		
CO ₃ ²⁻						2.40	1.40	1.40	1.27	0.13	1.16	
CoCO ₃						2.00						2.00
NaCO ₃ ·10 H ₂ O									5.52			
Total	999.75	999.54	199.45	200.15	199.95	40.03	40.25	38.25	34.81	3.44	5.52	2.00

Figure 2.8: Conceptual flowsheet for Co recovery from water using the IL [P₈₈₈₈][Oleate] for extraction and a 1 M Na₂CO₃ solution for regeneration.

2.5 CONCLUSIONS

Using the hydrophobic ionic liquid $[P_{8888}][\text{Oleate}]$, the proof-of-principle of a new process for metal ions removal from water has been demonstrated. The extraction efficiency of Co was above 99 % and by using $\text{Na}_2\text{CO}_3(\text{aq})$ as regeneration solution up to 98% of the initially present Co in the feed was recovered as $\text{CoCO}_3(\text{s})$, being a marketable product. The proposed process is most interesting for the selective recovery of metals and can accommodate any HIL that shows selectivity, can be regenerated, and has a low loss rate to the aqueous phases. $[P_{8888}][\text{Oleate}]$ already shows selectivity, though under extreme pH conditions. Furthermore, it has a low loss rate to the aqueous phases.

By performing five extraction-regeneration cycles it became evident that the measurement of a single extraction-regeneration cycle is not sufficient to perceive conclusive information about the steady state conditions of the process with respect to efficiencies, recoveries, and ion transfer mechanism. The case discussed in this chapter shows the need for multiple subsequent extraction-regeneration cycles as a sound basis for process development.

APPENDIX 2.A

CYCLIC EXPERIMENTS

A feed solution was prepared with a concentration of 1 g/L cobalt and sodium from their corresponding chloride salts. Sodium carbonate was applied as regeneration solution in different concentrations (0.3-1.0 M). For the first extraction cycle, 5 ml of this solution was added to 5 ml of water-saturated $[P_{888}][\text{Oleate}]$ and mixed at room temperature for 2 hours using a Heidolph Multi Reax vortex mixer at a speed of 2500 rpm. During the first three cycles the volume ratio was unity while for the fourth and fifth cycle the ratio changed because the limited amount of IL available and the reduction over time due to sample taking for analysis. Table 2.A.1 shows the volumes of feed, aqueous phase for regeneration and IL used in the five subsequent cycles.

Table 2.A.1: Volumes of feed $V_{f,i}$, aqueous phase for regeneration $V_{RF,i}$ and IL $V_{IL,i}$ used during each of the five extraction and regeneration cycle.

Na ₂ CO ₃ Concentration (M)	Volume (mL)									
	Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
	$V_{f,i}/V_{RF,i}$	$V_{IL,i}$	$V_{f,i}/V_{RF,i}$	$V_{IL,i}$	$V_{f,i}/V_{RF,i}$	$V_{IL,i}$	$V_{f,i}/V_{RF,i}$	$V_{IL,i}$	$V_{f,i}/V_{RF,i}$	$V_{IL,i}$
0.3 M	5.00	5.00	4.18	4.18	3.08	3.08	3.50	2.35	3.50	1.40
0.5 M	5.00	5.00	4.31	4.31	3.44	3.44	3.50	2.49	3.50	1.78
0.7 M	5.00	5.00	4.29	4.29	3.36	3.36	3.50	2.51	3.50	1.72
1.0 M	5.00	5.00	4.28	4.28	3.25	3.25	3.50	2.47	3.50	1.72

Figure 2.A.1 shows the results of five consequent extraction and regeneration cycles. The dotted-line peaks of the fifth cycles are (about) twice in height compared to the peaks of cycles 1-3, resembling the applied IL: feed volume ratio of 1:2 and 1:1, respectively. To allow a fair comparison with the first three cycles and assuming an extraction efficiency independent of the IL:feed volume ratio (see Figure 2.A.1), the solid lines in Figure 2.A.1 show the calculated Co concentrations after normalizing the data for the fourth and fifth cycle for a volume ratio of 1:1. Based on these normalized plots, it is concluded that with 0.5 M and 0.7 M Na₂CO₃ as regeneration solution steady-state was reached from the second cycle on, whereas with 1 M Na₂CO₃ steady-state was reached already from the first cycle on. Furthermore, measured cobalt concentration in feed, raffinate, lean (regenerated) IL and regeneration raffinate during extraction and regeneration process in five cycles are tabulated in Table 2.A.2.

Figure 2.A.1: (Normalized) Cobalt concentration in the HIL after extraction and regeneration during 5 cycles, using Na_2CO_3 solutions of either 0.5 M (A), 0.7 M (B) or 1.0 M (C). The SD of the measured cobalt concentration in the feed is 12 mg/L resulting in a same SD for the calculated cobalt concentration in the IL of 12 mg/L. The error of $2 \times \text{SD} = 25$ mg/L. Error analysis assuming an error of $2 \times \text{SD} = 24$ mg/L in the feed concentration and 2.5% in the volume resulted in an error of 5% in the normalized concentration. Note the different volume ratios $V_{\text{IL}}/V_{\text{aq}}$, ranging from 1:1 to 1:2, used for the several cycles. The dashed line for cycles 4 and 5 refers to raw data, the solid line to the same data but normalized for a $V_{\text{IL}}/V_{\text{aq}}$ ratio of unity (see text). Panel D shows the first regeneration step at the three different carbonate concentrations used. Clearly visible are the Co-containing, purple coloured upper IL phase and the solid CoCO_3 precipitate collected at the bottom of the tube.

Table 2.A.2: Measured cobalt concentration (mg/L) in feed $C_{f,o}$, raffinate $C_{r,i}$, lean (regenerated) IL $C_{l,i}$, and regeneration raffinate $C_{rr,i}$ during extraction and regeneration process in five cycles.

[Na ₂ CO ₃] (M)	Concentration of cobalt (mg/L)																								
	Cycle 1					Cycle 2					Cycle 3					Cycle 4					Cycle 5				
	C _{t,o}	C _{r,i}	C _{LeI,L}	C _{RR,j}	C _{r,i}	C _{r,i}	C _{LeII,L}	C _{RR,i}	C _{r,i}	C _{LeLI}	C _{RR,i}	C _{r,i}	C _{LeLI}	C _{RR,j}	C _{r,i}	C _{LeLI}	C _{RR,j}	C _{r,i}	C _{LeLI}	C _{RR,j}	C _{r,i}				
0.3 M	984	2.30	638.67	8.70	9.04	489.15	9.42	4.06	256.23	5.00	2.50	117.67	5.00	2.50	108.88	5.00	2.50	108.88	5.00	2.50					
0.5 M	984	2.40	248.43	21.40	17.30	199.73	9.78	3.28	142.11	6.86	2.50	80.38	7.10	2.50	148.70	7.40	2.50	148.70	7.40	2.50					
0.7 M	984	2.50	128.81	39.60	2.03	251.23	13.18	2.50	89.27	8.76	2.50	78.73	9.34	2.50	23.33	6.64	2.50	23.33	6.64	2.50					
1.0 M	984	2.30	39.11	5.00	0.50	50.98	15.82	2.50	59.96	0.07	2.50	89.86	14.72	2.50	60.68	14.70	2.50	60.68	14.70	2.50					

APPENDIX 2.B

ANALYSIS OF COBALT PRECIPITATE

The composition of the formed precipitate was evaluated using Energy Dispersive X-ray fluorescence spectrometry (EDX) and Scanning electron microscopy (SEM). Results are shown in Figure 2.B.1 and 2.B.2, respectively. The main component of each composite was cobalt and oxygen with a ratio of 1 to 3, which confirms the initial hypothesis that the produced precipitate is indeed cobalt carbonate. The weight percentage (wt.%) of cobalt in the solid product is around 45%, whereas impurities (i.e., sodium and phosphorus) make out less than 1 %. This weight percentage is in agreement with the commercial product where cobalt wt.% ranges between 43-47%. [24]

Figure 2.B.1: SEM-EDX analysis of the granular precipitate “ CoCO_3 ”, measured during 500x magnification. Please note that the Au originated from the pre-preparation of the sample prior to SEM-EDX analysis.

Figure 2.B.2: SEM image of granular cobalt carbonate as precipitated during IL regeneration with sodium carbonate solutions. Magnification of image A: 2500, image B: 10000.

The precipitate was also analysed using Raman Spectroscopy (see Figure 2.B.3). By comparing the obtained data with the CoCO_3 Raman Spectra of several CoCO_3 suppliers, it was found that the formed CoCO_3 has the same characteristic bands as those in the literature. In Figure 2.B.3, cobalt carbonate is represented by the sharp peak at 1075 cm^{-1} . Bands present in the low frequency region, specifically at 463 , 531 and 600 cm^{-1} , are assigned to spinal cobalt oxide, Co_3O_4 . Occurrence of these spikes in the spectrum of CoCO_3 are generally due to lattice vibrations and liberations. [24, 27, 28]

Figure 2.B.3: Raman spectrum of the formed cobalt carbonate during IL regeneration. Plots are enlarged and offset to show low intensity features.

APPENDIX 2.C

ION TRANSFER

Figure 2.7 in the main text refers to the use of 0.1 M $\text{Na}_2\text{CO}_3(\text{aq})$ as regeneration solution. Here we show similar data but for a 1 M $\text{Na}_2\text{CO}_3(\text{aq})$ regeneration solution.

Figure 2.C.1: Absolute amount of ion species **exchanged** (in μmol) between aqueous (CoCl_2) and organic IL phase during extraction, calculated for the first and second cycle. The intermediate regeneration step was performed with 1 M $\text{Na}_2\text{CO}_3(\text{aq})$. Panels A) and B) refer to an IL with (A) and without 20% excess oleate (B).

Nomenclature

Symbols	Description	Unit
$C_{f,o}$	Co concentration in the feed	g/L
$C_{r,i}$	Co concentration in the raffinate - cycle i	g/L
$C_{LeIL,i}$	Co concentration in the lean IL - cycle i	g/L
$C_{LeIL,i-1}$	Co concentration in the lean IL - cycle i-1	g/L
$C_{LoIL,i}$	Co concentration in the loaded IL - cycle i	g/L
$C_{RR,i}$	Co concentration in the regeneration raffinate - cycle i	g/L
$V_{f,i}$	Volume of the feed - cycle i	L
$V_{IL,i}$	volume of IL phase – cycle i	L
$V_{RF,i}$	Volume of regeneration feed – cycle i	g/L
$R_{CoCO_3(s),i}$	Co recovery per cycle i	%
$R_{CoCO_3(s),j}^*$	Co cumulative recovery form cycles $i=1$ to $i=j$	%

Greek letters

$\eta_{E,i}$	Extraction efficiency for cycle i	%
$\eta_{R,i}$	Regeneration efficiency for cycle i	%

Subscripts

aq	Aqueous phase
IL	Ionic liquid
HIL	Hydrophobic ionic liquid
LLX	Liquid- liquid extraction

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CHAPTER 3

RECOVERY OF METALS FROM SPENT LITHIUM-ION BATTERIES USING IONIC LIQUID [P₈₈₈₈][OLEATE]

Everything is theoretically impossible until it is done

Robert A. Heinlein

ABSTRACT

A separation method to selectively recover valuable metals (Co, Ni, Mn and Li) from synthetic spent lithium-ion battery cathodes leachate using a fatty-acid-based ionic liquid, tetraoctylphosphonium Oleate [P_{888}][Oleate] is demonstrated. The investigated parameters for this selective separation and recovery process include extraction pH, contact time and composition of the regeneration solution. The benefit of using this ionic liquid is that > 99 % of Co and > 99 % of the Mn can be separated from the Ni and the Li by a two-stage extraction process. A subsequent single regeneration process separates the Co from the Mn. Finally, Ni and Li are completely separated in an additional regeneration process. An economic potential analysis concludes the chapter, revealing that given the current Co price, the process outlined here shows a positive zero-order Economic Potential (bases on product sales and raw material cost) when using a 4 M HCl leaching solution and for leachates containing at least 4.5 g Co per liter.

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3.1 INTRODUCTION

In lithium-ion battery (LIB) technology, the use of multi-metal cathodes such as lithium-nickel-manganese-cobalt oxide (NMC) has become customary in order to reduce cost, to stabilize raw material supply chains, to increase energy density and battery performance [1-6]. To date, 95% of Li-ion battery waste is landfilled instead of recycled upon reaching end of life [7]. Even though metal recycling is by far the preferable option from the point of view of future economy, environment and human health [8]. Selective metal recovery is however challenging in terms of heterogeneity of the waste material, necessary degree of purity of the recovered metals and sustainability of the overall recycling process [9-11].

Currently, the two most widely used processes for the treatment of spent LIB's are hydrometallurgical and pyrometallurgical in nature. However, hydrometallurgical processes consume less energy, show a higher metal recovery rate with high purity and seem more adjustable for recycling future generations of LIBs [12, 13]. After a series of pre-treatment steps such as discharging, dismantling, crushing and sieving, the different valuable cathode metals are separated by leaching using strong acids or bases, followed by purification steps like solvent extraction, precipitation, electrolytic processing or a combination of these methods [14, 15]. However, the efficiency of (selective) metal precipitation is limited because the process is time-consuming, due to the co-precipitation of other more concentrated metals and finally due to the low yield of metal precipitation (< 50%) [15]. Furthermore, the process may require the use of an additional chemical reagent, e.g. dimethylglyoxime as in the case of nickel recovery [15]. Solvent extraction-based techniques are considered to be more efficient, because they allow operation in the continuous mode, require relatively simple equipment along with relative small quantities of reagents while still achieving a high leachate throughput [16]. In addition, liquid-liquid extraction (LLX) processes are in general rather flexible towards the nature and concentration of the extractants and the composition of the aqueous and organic phase [17].

Currently used metal extractants include Cyanex 272 (di-isooctyl phosphinic acid), PC88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester), and D2EHPA (di-2-ethylhexyl phosphoric acid) [12, 18-20]. The main disadvantage of these commercially available extractants is the required use of a highly toxic diluent like kerosene. Secondly, multiple extractants are needed to selectively recover valuable metals from spent LIBs such as NMC leachates which contain cobalt (Co), manganese (Mn), nickel (Ni) and lithium (Li) [21]. For example, Cyanex 272 and PC88A are mainly used to separate Co from Ni while D2EHPA is used to separate Co from Mn [12, 21]. Furthermore, in the extraction of metals by saponified extractants, which show better separation compared to non-saponified ones, stripping with strong acid may convert the saponified extractant into its acid

form, which in turn will decrease the extraction of metals [22]. Therefore, an additional regeneration step is employed to convert the acid form of the extractant to the saponified form. Considering the wide ranges of specifications and with that realizing the limitation of comparison, Table 3.1 lists currently employed organophosphorus extractants used in the separation of Co, Mn and Ni. In order to circumvent the use of kerosene, to reduce the number of stages/extractants involved in the process and accordingly to reduce the environmental impact, the present study explores the applicability of an ionic liquid (IL) as a viable alternative to selectively recover Co, Mn, Ni and Li from a synthetic leach solution originating from cathodic material of spent LIBs (NMC). Even though the viscosity of this IL is 0.134 Pa.s, it is applicable in its pure, undiluted form.

Table 3.1: Comparison of Co/Ni separation factors and cost for various extractants. Selectivity is defined as $\beta_{Co/Ni} = D_{Co}/D_{Ni}$, where D_M is distribution coefficient of metal (M) = $(C_{f,o} - C_{r,i})/C_{f,o}$.

Extractant	Price (\$/kg)	$\beta_{Co/Ni}$	Concentrations (g/L)	Diluent	Ref
Cyanex 272	1-160*	750	[Co]=14, [Ni]=15	kerosene	[19]
PC88A	6-8*	42	[Co]=21, [Ni]=1	kerosene	[23]
D2EHPA	2-30*	14	-	kerosene	[24]
[P₈₈₈₈][Oleate]	10**	30000	[Co]=15, [Ni]=21	-	This study

*Price according to Alibaba 20 Oct 2019 which varies with supplier, quality and quantity.

** Price for [P₈₈₈₈][Oleate] has been calculated based on raw material costs only, as shown in (Appendix 3.A).

As shown in numerous studies already, ILs can be designed accordingly to the metal they need to extract [25-33]. One such IL is tetraoctylphosphonium oleate [P₈₈₈₈][Oleate] (Figure 3.1), a metal-binding functionalized fatty-acid-based IL that demonstrates a high and selective extraction efficiency towards transition metals at different pH levels [34]. The presence of bulky, long chained tetraalkylphosphonium cations and hydrophobic oleate anions prevent the loss of IL to the aqueous phase. The latter, anion loss after protonation, occurring when exposed to an acidic feed or an acidic regeneration solution, is a commonly observed feature with IL's composed of a conjugated acid and an anion such as phthalate [25, 26]. Because of its bulky nature, protonation of the oleate anion hardly affects its hydrophobicity, thereby preventing its loss to the aqueous phase.

Figure 3.1: Tetraoctylphosphonium oleate [P_{8888}][Oleate].

The focus of the present study is on the extraction and regeneration efficiency of [P_{8888}][Oleate] for the four metals Co, Mn, Ni and Li during 2 cycles of operation. Several parameters affecting these efficiencies have been investigated, notably pH, contact time, composition of the regeneration solution and number of required extraction/regeneration stages within one cycle. At the end, the outcome of a (simplified) economic analysis (based on product sales and raw material cost = EP0) of the process outlined here is discussed.

3.2 EXPERIMENTAL

3.2.1 MATERIALS AND ANALYSIS

Tetraoctylphosphonium bromide (> 95 %) was purchased from IoLiTec; sodium hydroxide (>99 %), hydrochloric acid (37 %), nitric acid (69 %), ammonia solution (minimum 25 %), ammonium chloride, ammonium carbonate, sodium chloride, sodium hydrogen carbonate and sodium carbonate from VWR Chemicals; oleic acid (90 %), nickel (II) chloride hexahydrate (99.95%), cobalt (II) chloride hexahydrate (98 %) and ammonium bicarbonate (99.0 %) from Alfa Aesar; ammonium sulphate, perchloric acid (70%), lithium chloride (99 %) and manganese (II) chloride dihydrate (99 %) from BOOM BV. MilliQ water (≥ 18 M Ω .cm) was obtained from a Millipore Milli-Q® Biocel, which uses a Qgrade® column. All chemicals were used as received, without any further purification.

The aqueous phases after each extraction and regeneration process were analyzed by a Metrohm IC Compact 761 ion chromatograph (detection range: 0.1 - 80 mg/L) and a Perkin Almer Optima 5300 DV inductive coupled plasma optical emission spectrometry (ICP-OES) (detection range: 0.05 - 10 mg/L). The organic phase was digested using a Milestone Ethos. The pH of feed, regeneration and raffinate solutions have been measured using a Mettler Toledo pH-meter which works in the range of -2 to 20 with an accuracy of ± 0.002 .

Recovered metal precipitate were evaluated using Fourier transform infrared spectroscopy (FTIR). Easy microwave digester (Appendix 3.B) and analyzed using the same instruments as applied for the aqueous phase.

3.2.2 SYNTHESIS AND ANALYSIS OF $[P_{888}][OLEATE]$

Tetraoctylphosphonium oleate $[P_{888}][Oleate]$ was synthesized according to the procedure described in chapter 2 with some modification [27]. Briefly, sodium oleate was produced by adding oleic acid (52.36 g, 0.19 mol) to 800 mL of sodium hydroxide (12.74 g, 0.32 mol). After stirring at 45°C for 3 hrs., tetraoctylphosphonium bromide (100 g, 0.18 mol) was added and the stirring continued for 6 hours at 75 °C. The organic phase of the mixture was then washed with warm water (8 x 1 L) at 45 °C to remove sodium bromide and excess of sodium hydroxide. A slightly yellow viscous liquid was obtained after drying the IL under vacuum at 50 °C. The dried $[P_{888}][Oleate]$ was then saturated with water by mixing 10 wt.% of MilliQ water for 24 h at room temperature. After removal of the remaining water, the water content of the saturated $[P_{888}][Oleate]$ was measured by a coulometric Karl Fischer titrator (Mettler-Toledo, model DL39). The physical properties of the produced IL at room temperature are density: 0.894 g/ml; pH: 9.7; conductivity: 150 μ S/cm; viscosity: 0.134 Pa.s. The purity of the IL was determined using 1H NMR on a 400 MHz Bruker nuclear magnetic resonance (NMR) spectrometer (model: Avance III 400 MHz) and the following was determined within 2% error from theoretical NMR spectra : 1H -NMR (400 MHz, $CDCl_3$, ppm), δ 5.35 (2H, m), ~2.8 (+ ~2H, b, water), 2.40 (12H, m), 2.21 (2H, t, J=7.7Hz), 2.01 (4H, m), 1.59 (2H, m), 1.50 (14H, m), 1.30 (50H, d), 0.90 (15H, t, J = 6.8 Hz). Detection of synthesis impurities such as bromide and sodium were accomplished via Milestone Ethos Easy microwave digester and Metrohm IC Compact 761 Ion Chromatograph (measuring range: 0.10 – 80 mg/L).

3.2.3 METAL EXTRACTION AND REGENERATION PROCEDURE

The Co concentration in the (synthetic) feed solution was set at 1 g/L (in line with experimental work presented in chapter 2) [27]. As for the other metals, we followed the weight ratios presented by Hu et al., (Table 3.2) [35], resulting in 1.14 g/L Mn, 1.40 g/L Ni and 0.39 g/L Li. All the metals were added as chloride salts. Unless stated otherwise, standard feed solution with the above composition was prepared without pH adjustment. Then, 5 mL of the feed solution was added to 5 mL of the water-saturated IL $[P_{888}][Oleate]$ (around 10 wt. % water) and mixed for 5 min at 40 rpm unless stated otherwise (Appendix 3.C). After centrifugation for 10 min at 3750 rpm (22 °C), in an Allegra X-12R Centrifuge of Beckman Coulter. The loaded IL was regenerated with 5 mL of various concentrations single or multi sodium and ammonium salt solutions for 2 hours and centrifuged (3750 rpm; 10 min, 22°C). Sodium salts used as regeneration solutions are sodium carbonate Na_2CO_3 , sodium nitrate $NaNO_3$, sodium phosphate Na_3PO_4 and sodium sulphate Na_2SO_4 . Ammonium salts are ammonium hydroxide NH_4OH , ammonium chloride NH_4Cl ,

ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, ammonium bicarbonate NH_4HCO_3 . Concentrations and compositions are defined in more detail in (Appendix 3.D).

Table 3.2: Main components, accounting for ~60 % of total mass, in the spent lithium ion battery cathodes [35]. Oxygen (not shown) contributes for another 21 wt.%, other elements for the remaining part.

Element	Co	Li	Ni	Mn
Wt. [%]	14.88	5.75	21.87	16.96

The extraction efficiency ($\eta_{E,i}$), with equal volumes of aqueous and organic phase, in cycle i is calculated by:

$$\eta_{E,i} = \frac{(C_{f,o} - C_{f,i})}{C_{f,o}} \times 100 \% \quad (3.1)$$

The regeneration efficiency ($\eta_{R,i}$) is calculated by:

$$\eta_{R,i} = \left(1 - \frac{C_{LeIL,i} V_{IL,i}}{(C_{f,o} - C_{f,i}) V_{f,i} + C_{LeIL,(i-1)} V_{IL,i}} \right) \times 100 \quad (3.2)$$

3.3 RESULTS AND DISCUSSION

3.3.1 OVERALL SEPARATION AND RECOVERY PROCESS

Figure 3.2 shows a flow diagram of the overall metal extraction and recovery process, which will be discussed in more detail in the next sections. It is important to mark the difference between cycle and stage. Here, cycle refers to (repeating) the whole process of extraction and regeneration, whereas stage refers to (repeating) a single step more than once (each time using fresh organic phase in extraction or fresh regeneration solution in regeneration) during a cycle to enhance either the extraction or regeneration efficiency. The entire process was carried out for two subsequent cycles with 5 min and 2 hrs for each extraction and regeneration stage, respectively. The regenerated IL from the first extraction stage was reused in the extraction stage of the 2nd cycle. Abbreviations, like E-1, R-1-A, Rf-1, used throughout the text refer to Figure 3.2.

3

3

3

Figure 3.3: Extraction efficiency of cobalt, manganese, nickel and lithium using $[P_{888}]$ [Oleate] as a function of the pH of initial metal feed solution.

At pH 5, Co, Mn and Ni are extracted as aqua complexes with high efficiency of nearly 100% via the anionic part of the IL (oleate) as suggested by Parmentier et. al., (2016) for an ammonium-based ionic liquid (Eq. 3.3), while Li is essentially not extracted at all [38]. Compared to the extraction at pH 5, the lower extraction observed at pH 0.43 - 0.1 reflects an effect most likely due to the high HCl concentration in the feed and the consequential increased extraction of HCl into $[P_{888}][Oleate]$ [31]. As a result, the oleate anions of the IL become protonated and with that are no longer available for extraction [34]. Using 8 M HCl, the extraction efficiency of Co and Mn, but not of Ni, starts to increase again at pH < 0 to reach 99% and 89% for Co and Mn, respectively. This behaviour reflects the formation of negatively charged tetrachlorocobaltate(II) and tetrachloromanganate(II) complexes in the presence of excess chloride ions and the extraction of these metal complexes by the cationic part of the IL (Eq. 3.4) [34]. The same behaviour has been observed in the extraction of copper using carboxylic acid based hydrophobic eutectic solvents as reported by Schaeffer et al., [33].

pH > 0.5

pH < -0.5

In contrast, the stability of the negatively charged nickel-tetrahedral chloro-complex is relatively low compared to Co and Mn based on the stability constant as shown in Table 3.3 [39, 40], This results in a very low extraction efficiency of Ni around 3% (Figure 3.3).

Note that in the pH range studied Li is essentially not extracted at all, in accordance with a previous study showing that the extraction of alkali metals like Li require alkaline conditions [34]. This differential behaviour towards pH thus offers the possibility to effectively separate Co and Mn from Ni and Li. Therefore, the extraction of Co and Mn was carried out starting from a highly acidic 8 M HCl feed solution of pH<0.

Table 3.3: Overall stability constants of metal chloro-complexes in aqueous feed solution [40].

Metal chloro-complex	log β_4
$[\text{CoCl}_4]^{2-}$	8.2
$[\text{MnCl}_4]^{2-}$	6.7
$[\text{NiCl}_4]^{2-}$	2.8

Table 3.4 shows extraction efficiencies during the two subsequent cycles of 99% and 89-84% for Co and Mn, respectively. The overall extraction of Ni and Li remains < 4%. Compared to Co, the extraction efficiency of Mn is relatively modest. As will be discussed in the ‘process optimization’ section 3.3.3, a second extraction stage can recover the residual Mn remaining in Raffinate-1 (Rf-1).

Table 3.4: Single stage extraction efficiencies of metals from a highly acidic chloride medium (8M).

Metal	$\eta_{E,i}$			
	Co	Mn	Ni	Li
Cycle 1	99	89	4	3
Cycle 2	99	84	2	2

The data clearly show that during two subsequent cycles of operation, the extraction efficiency of Co remains essentially unaffected whereas the extraction of Mn lowers by about 5%. Most likely, this reduction is (partly) caused by a slightly lower IL: feed ratio, due to the IL sample taken for analysis. Apparently, the Co extraction efficiency is less sensitive to the IL: feed ratio. While the extraction efficiencies of Ni and Li remain less than 4%. From these results we conclude that the $[\text{P}_{888}][\text{Oleate}]$ is fairly stable, even during exposure to feed solutions of pH<0. By implication, $[\text{P}_{888}][\text{Oleate}]$ can be used during subsequent extraction and regeneration stages.

3.3.1.2 SEPARATION AND RECOVERY OF COBALT AND MANGANESE (R-1-A & B)

Regeneration solutions of different composition and ionic strength were tested for their regeneration efficiency. The finally selected regeneration solution is a composite of 1M NH_4OH , 1.2M $(\text{NH}_4)_2\text{CO}_3$ and 1M $(\text{NH}_4)_2\text{SO}_4$. The selection of this particular composite required the screening of a range of single and multi-salt solutions for their regeneration

efficiency, including the effect of their (relative) concentration. For brevity and in order not to hamper the flow of the paper, these data are summarized in (Appendix 3.D). Figure 3.4 shows the results of four promising regeneration solutions. After establishing the ideal combination, the relative amounts were fine-tuned. A distinction was made between the relative amount of the recovered metal appearing in solution and as precipitate. Clearly, solution RS-2 is the regeneration solution of choice because it combines 100% efficiency for Co (purity 97%) with >90% of Mn of which by far the largest part precipitates (purity 94%), thereby separating the two metals. Even though the two metals thus can be effectively separated, 90% recovery of Mn requires a two-stage regeneration, whereas for Co a single stage suffices for 100% yield. RS-2 recovers Co in the form of an (dissolved) aqueous amino complex and Mn as a precipitate of MnCO_3 .

Figure 3.4: Two-stage (total) regeneration efficiency for Co and Mn using regeneration solutions (RS) possessing a combination of three salts: NH_4OH , $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{SO}_4$ differing in (relative) concentration. RS-1: 1 M NH_4OH , 1.1 M $(\text{NH}_4)_2\text{CO}_3$ and 0.9 $(\text{NH}_4)_2\text{SO}_4$. RS-2: 1M NH_4OH , 1.2M $(\text{NH}_4)_2\text{CO}_3$ and 1 $(\text{NH}_4)_2\text{SO}_4$. RS-3: 1M NH_4OH , 1.3M $(\text{NH}_4)_2\text{CO}_3$ and 1.1 $(\text{NH}_4)_2\text{SO}_4$. RS-4: 1M NH_4OH , 1.4M $(\text{NH}_4)_2\text{CO}_3$ and 1.2 $(\text{NH}_4)_2\text{SO}_4$. Light and dark bar areas indicate metal in solution and metal as precipitate, respectively.

Regeneration solution RS-2 (1M NH_4OH , 1.2M $(\text{NH}_4)_2\text{CO}_3$ and 1 $(\text{NH}_4)_2\text{SO}_4$.) not only serves to recover the metals (and regenerate the IL) but also to separate the two metals Co and Mn. Reaction schemes 5-7 outline a possible scenario of complex formation and conversion during regeneration. The sequence of complex formation is based on colour identification as described in the literature and shown in Figure 3.5. It all starts with metal chloro-complexes (blue in Figure 3.5-B IL) changing to cobalt chloride dihydrate (purple in Figure 3.5-C IL), indicating ligand exchange between the IL and the alkaline regeneration solution [41, 42]. The ligand exchange reaction, essentially the neutralization of the organic phase, can be expressed as:

Figure 3.5: Ionic liquid in different states. (A) pure IL, (B) loaded IL with $[CoCl_4]^{2-}$ and $[MnCl_4]^{2-}$ complexes, (C) neutralized loaded IL (first 5 min of regeneration) and (D) fully regenerated IL. RRf: regeneration raffinate.

Once in the ammonia-ammonium containing regeneration solution, the metal complexes undergo further ligand exchange. The cobalt aqua complex exchanges water for ammonia - (Eqs. 3.6 and 3.7) to form hexamminecobalt (II) complex, initially pink in colour (Figure 3.5-C RRf). This complex forms a deep-red solution after full regeneration of loaded ionic liquid (Figure 3.5-D RRf) which is soluble in Regeneration Raffinate (RRf-1-A) [43, 44]. The manganese aqua complex reacts with carbonate forming a manganese carbonate precipitate (PPT-1-A), thereby phase-separating from the cobalt-containing raffinate:

Table 3.5 shows the regeneration efficiency of Co and Mn during two consecutive cycles. Using RS-2, in the first regeneration stage (R-1-A), the regeneration efficiency of Co and Mn is 100% and 80%, respectively. In order to enhance the Mn regeneration, a second regeneration stage was deployed, using 2 M $(NH_4)_2CO_3$ (R-1B), resulting in a total (RRf+PPT) Mn regeneration efficiency of 93% for the first cycle versus 92% for the second cycle. Precipitates in Figure 3.2 are indicated in red. FTIR spectra of $MnCO_3$ precipitate matches that found in literature (see Appendix 3.E) [45]. Even though not included in this study, as for harvesting Co in the form of metallic Co or Co_nX_n (printed in blue in Figure 3.2), X_n depends on the technology used for the Co recovery section. For example, electrodeposition renders metallic Co, roasting CoO and heating in acidic conditions $CoCl_2$ [46, 47].

Table 3.5: Regeneration efficiency of Co and Mn as dissolved complex in the regeneration raffinate (RRf) and as solid precipitate (PPT) during the first stage (1-A) and second stage (1-B) regeneration for two cycles.

Metal	$\eta_{R,i}$							
	RRf-1-A		PPT-1-A		RRf-1-B		PPT-1-B	
	Co	Mn	Co	Mn	Co	Mn	Co	Mn
Cycle 1	100	2	-	80	-	3	-	9
Cycle 2	100	4	-	75	-	4	-	8

3.3.1.3 EXTRACTION OF NICKEL (E-2)

With Ni and Li left behind in raffinate Rf-1 (Figure 3.2), the next step is to separate these two metals. Prior to the second extraction process, a pH adjustment to less acidic conditions (pH 1-2) with NaOH is needed to prevent the protonation of oleate during extraction. This leaves way for Ni to be extracted by interacting with the anionic part of the IL, as discussed in section 3.3.1.1.

Table 3.6 shows that a single stage extraction of 5 minutes duration is sufficient to extract all the Ni from Rf-1. Remarkably and in contrast to the data shown in Figure 3.3, a substantial amount of Li is co-extracted. For now, the most plausible explanation is that the extraction of Li reflects the salting out effect of Na which results from the addition of NaOH for pH adjustment. Finally, Li can be recovered as Li_2CO_3 from Rf-2 via evaporation using saturated Na_2CO_3 .

Table 3.6: Extraction efficiency of Ni and Li at pH=1.

Metal	$\eta_{E,i}$	
	Ni	Li
Cycle 1	100	33
Cycle 2	100	25

3.3.1.4 SEPARATION AND RECOVERY OF NICKEL AND LITHIUM (R-2)

The regeneration of Ni and Li from the loaded IL was accomplished using 1 M Na_2CO_3 in a single stage for 2 hrs. This regeneration process resulted in the separation of Ni from Li via the formation of NiCO_3 precipitate (PPT-2 in Table 3.7) leaving the co-extracted Li in the regeneration Raffinate 2 (RRf-2). This is due to the difference in solubility product of NiCO_3 (1.42×10^{-7}) and Li_2CO_3 (8.15×10^{-4}) [48]. In order to increase the precipitation of NiCO_3 , the IL used in the first extraction cycle (E-2, cycle 1) needs to be pre-saturated with Na_2CO_3 . Without this initial saturation step of the IL with Na_2CO_3 , Ni extraction leads to a lower regeneration efficiency of 80% and reduces precipitation to 51%. The purity of

the produced NiCO_3 precipitate is around 100% and its FTIR spectrum is in line with that obtained for standard sample (see Appendix 3.E).

Table 3.7: Regeneration efficiency of Ni and Li, partly dissolved in the regeneration raffinate (RRf-2) and partly precipitated (PPT-2).

Metal	$\eta_{R,i}$			
	RRf-2		PPT-2	
	Ni	Li	Ni	Li
Cycle 1	4	81	94	3
Cycle 2	4	88	94	-

The regeneration raffinate (RRf-2), containing Na_2CO_3 and Li_2CO_3 , can be recycled over the regeneration process to increase the lithium concentration to a value close to its solubility limit. The lithium salt in the regeneration raffinate (RRf-2) could be obtained via evaporation of water.

3.3.2 SELECTIVITY AND CAPACITY OF $[\text{P}_{888}][\text{OLEATE}]$

As shown, with 1 g of Co/L and 1.14 g of Mn/L present in the feed, $[\text{P}_{888}][\text{Oleate}]$ extracts Co about 10% more efficient than Mn (Table 3.4), resulting in an extraction ratio of Co and Mn of around 10:9. Increasing the feed concentrations of both metals to 5 g/L Co significantly shifts this ratio in favor of Co, resulting in a Co:Mn extraction ratio of approximately 2:1. This ratio further increases to 5:1 with 10 g/L Co and to 6:1 with 15 g/L Co in the feed (Figure 3.6). The corresponding Mn concentrations are given in the legend of Figure 3.6.

Figure 3.6: Extraction efficiency of Co and Mn at different initial feed concentrations of both ion species: 1, 5, 10 or 15 g/L (Co) and 1.14, 5.7, 11.4 and 17.1 g/L (Mn). Experimental conditions: 8 M HCl, T= 22 °C.

In brines containing higher concentrations of both metals this behaviour can be exploited as it (partly) shifts the separation of Co and Mn from the regeneration to the extraction phase. The preference for Co points to an intrinsic (concentration-dependent) Co over Mn selectivity of $[P_{888}][Oleate]$. The reason for this preference goes back to the atomic level. Even though they are very similar, Co and Mn do differ in ionic radius as well as charge density [49, 50]. With 58 pm (Co) and 66 pm (Mn), Co is the smallest of the two and with that has the highest charge density. Because of this and because Co is slightly more electronegative (25.28) than Mn (24.40), Co may have a higher propensity to form complexes with Cl as shown in Table 3.3, which are, in addition, more stable than those based on Mn [49, 50]. Figure 3.6 also indicates the high capacity of this IL to take up metals, especially, Co. With 15 g/L Co present in the feed and an extraction efficiency of around 61%, the uptake of Co amounts to 9 g per liter IL.

3.3.3 PROCESS OPTIMIZATION

Discussing ways to optimize the process demands, first, a definition of optimization, is it in terms of extraction efficiency, cost or, for example, environmental impact. Obviously, these different definitions and approaches may lead to a totally different outcome. A hundred percent extraction is preferred, of course, but against what cost? Cost reduction might be achieved by one-stage instead of two-stage extraction and limited regeneration processes, but the compromise is a metal containing waste stream. From the point of view of environmental impact, it is also not evident how to optimize the process. Including a second extraction or regeneration stage may prevent metals ending up in a waste stream but what about the impact of the other chemicals needed to achieve this?

Therefore, process optimization was performed via reducing the amount of HCl to minimize the environmental impact and costs without compromising the extraction efficiency. A set of experiments were performed using different HCl concentrations of 4, 5, 6 and 8 M. Table 3.7 shows that when employing a single stage, the extraction efficiency increases from 79% using 4 M HCl to 99% using 8 M HCl for Co and from 39% to 90% for Mn. As previously remarked, this enhancing effect of increased acid molarity reflects the formation of negatively charged chloro-complexes in the presence of excess chloride, which in turn promote metal extraction [39]. As shown in Table 3.7, a second extraction stage can partially compensate for the lower extraction efficiency resulting from lowering the HCl concentration. This effect becomes more prominent at lower HCl molarity. For instance, when using 4 M HCl, introduction of a second stage increased the Co and Mn extraction efficiency from 79% to 89% and from 39% to 46%, respectively. In industry, this can be achieved by implementing multiple counter-current stages. An additional benefit of a second extraction stage is the reduction of metal impurities in Rf-1. When employing two-stage extraction, the extraction efficiency of both Ni and Li remained below 4%. From the economical point of view, a process including two-stage (or more) extraction at 4 M

HCl may turn out the preferred option. However, because $[P_{888}][Oleate]$ expresses its highest extraction efficiency during single stage at 8 M HCl, this higher HCl concentration has been selected for the experiments in this explorative study at laboratory scale.

Table 3.7: Extraction efficiency for Co and Mn at various HCl concentrations performed in two stages.

HCl (M)	pH	Metal	$\eta_{E,i}$		
			Stage-1	Stage-2	Total
4	-0.6	Co	79	47	89
		Mn	39	11	46
5	-0.7	Co	89	90	97
		Mn	46	62	73
6	-0.8	Co	97	99	99
		Mn	73	72	86
8	-0.9	Co	99	93	100
		Mn	90	100	100

3.4 ECONOMIC ANALYSIS

Even though the emphasis of the previous paragraph was on the optimization in terms of extraction efficiency, it is instructive to perform a (brief, high level) Economic Potential analysis (EP0), with EP0 defined as the difference between Sales and Feedstock cost.

$$EP0 = \text{Sales} - \text{Feedstock cost} \quad (3.8)$$

Sales and feedstock values are obtained by multiplying the process capacity/requirement (ton/year) by the sales price of cobalt and chemicals (\$/ton) respectively [51]. In the present study, metals other than Co were excluded from the EP0 analysis whereas the feedstock costs include leaching and neutralization reagents (HCl and NaOH respectively). As shown in Table 3.7 and discussed in the previous paragraph, both feed pH and number of extraction stages have a distinct effect on the (total) extraction efficiency.

Wang et al., argued that leaching 1 ton of spent LIB requires 50 m³ of 4 M HCl [52]. Based on this, the total cost for leaching and neutralization using 4 M HCl and NaOH becomes 7.1 k\$/ton spent LIB. The total income from recovered Co per ton spent LIB is 5.3 k\$ as based on a Co price of 35 \$ per kg (Investment Mine 6 month report, May 2019) and a Co concentration in the leachate solution of 3 g/L [53]. In this scenario, EP0 turns positive at a Co price of at least 48\$ per kg. Figure 3.7 presents the minimum Co price needed to obtain zero EP0 levels as function of the Co concentration, for four different leachate acidities. Evidently, apart from the molarity of the HCl used, increasing Co concentration in the

leachate will also shift the price of Co required for $EP_0=0$ to a lower value. For example, and as indicated in Figure 3.7, using 4 M HCl, reducing the volume by 33% (and with that increasing the Co concentration from 3 to 4.5 g/L), shifts the demanded minimum Co price from 48 to 33 \$ per kg. A further Co concentration increase by a factor 5 lowers the needed Co price to 12 \$ per kg.

Table 3.F.1 (Appendix 3.F) shows the economic potential analysis (EP_0) for 1 ton spent lithium ion battery leached in 10 and 50 m³ 4-8 M HCl (acidity after leaching). Note that the income from the recovery (for instance a gate fee for the spent LIB) and of other metals present (Ni for instance) is neglected. On the other hand, EP_0 does not take utility costs and depreciation into account. Even though the EP_0 analysis indicates that the process outlined here can in principle be transformed into economically feasible technology, up-scaling demands further optimization, for instance, in terms of utilizing counter current stages for both extraction and regeneration.

Figure 3.7: Co concentration (g/L) in the leachate as function of the Co price (\$/kg) needed for $EP_0=0$, at different molarities of the HCl used. Presented molarities refer to the value reached after the leaching process. The red solid line indicates the Co price as per May 2019 [53]. Red dashed lines present the Co concentration studied by Wang et al., [52] and the Co concentrations obtained after a volume reduction by a factor 2 and 5.

3.5 CONCLUSIONS

Using the phosphonium-based ionic liquid $[P_{888}][Oleate]$, Co, Mn, Ni and Li can be successfully separated and recovered from a simulated spent lithium-ion battery HCl-based leachate.

In a single-stage extraction at 8 M HCl (pH = -0.9), more than 99 % of the Co and 89% of the Mn can be extracted. The subsequent separation of Mn from Co can be achieved by a regeneration process using a composite solution containing ammonia, ammonium carbonate and ammonium sulphate and in which Co remains in the raffinate and Mn precipitates as MnCO_3 . The extraction efficiency of Mn can be improved to 99% by deploying a two-stage instead of a single-stage extraction process.

Next, using the same ionic liquid, the extraction of Ni can be achieved after increasing the pH to about 1, resulting in a low co-extraction of Li. Complete separation of Ni and Li can be accomplished by using a Na_2CO_3 solution during regeneration, due to the difference in the solubility product of both carbonate salts. The regenerated ionic liquid can be directly re-used in the subsequent extraction cycles.

The three key parameters defining the (possible) economic feasibility of the process outlined here are the Co concentration in the leachate solution, the molarity of the HCl used and the market price of Co. An EP0 analysis taking into account these parameters reveal that in terms of economics the use of 4 M HCl is preferred despite the fact that 8 M HCl showed the highest extraction efficiency for both Co and Mn. Furthermore, the break-even point, i.e. $\text{EP0}=0$ (at a current cobalt price of 35 \$/kg) can be reached by reducing the leachate volume by at least 33% and consequently increasing the cobalt concentration by 50 % to 4.5 g/L or once the cobalt price exceeds 48 \$ per kg.

APPENDIX 3.A

Table 3.A.1: Price calculation for IL [P₈₈₈][Oleate] based on raw material costs only.

Raw chemical prices in ton Scale*				
[P ₈₈₈][Br]	12	[\$ /kg]		
Oleic acid	1.1	[\$ /kg]		
NaOH	0.4	[\$ /kg]		
To synthesize 1 kg of IL (reaction yield of 95 %) we need:				
[P ₈₈₈][Br]	770	g	9.24	[\$]
Oleic acid	502	g	0.55	[\$]
NaOH	98	g	0.04	[\$]
Price per kg IL			9.83	[\$]

*Prices according to Alibaba.com, 22 October 2019

APPENDIX 3.B

Table 3.B.1: Microwave digestion trials.

Trial	T (°C)	IL mass (g)	Acid composition	% of undigested IL
1	180	0.25	2 mL H ₂ O ₂ + 8 mL HNO ₃	9.2
2	200	0.25	2 mL H ₂ O ₂ + 8 mL HNO ₃	42.0
3	200	0.25	1 mL HClO ₄ + 10 mL HNO ₃	23.0
4	220	0.1	1 mL HClO ₄ + 10 mL HNO ₃	0.5

MICROWAVE DIGESTION PROCEDURE FOR TRIAL 4

0.1 g of IL was weighted in a vessel and placed in a safety shield. 1 mL of 70 % HClO₄ and 10 mL of 69 % HNO₃ were pipetted into the vessel under a fume hood. Then, the vessel was closed with a Teflon cover along with an adaptor. The assembled vessel was then placed in a rotor segment and the screw on the segment was tightened. The procedure was repeated for other IL samples. Subsequently, all the rotor segments were distributed evenly in the microwave with one of them connected to a temperature sensor. Then, the microwave was set to running at 220 °C for 1 h. When the inner temperature reached ~25 °C, the vessels were removed from the microwave and the digested samples were diluted with Milli-Q water in 100 mL flasks. The diluted samples were analyzed using Shimadzu TOC-L Total Organic Carbon Analyzer to determine the percentage of undigested IL sample.

APPENDIX 3.C

EFFECT OF RESIDENCE TIME

Experiments aiming to investigate the effect of mixing time revealed that already 5 min (40 rpm, 22 °C) of mixing feed and IL (1:1) suffices to extract Co^{2+} , Mn^{2+} and Ni^{2+} with almost 100% efficiency. Lithium, on the other hand, remains in the raffinate, expressed by a low extraction efficiency of 4%, even after 20 min of mixing.

Figure 3.C.1: Effect of time on the extraction efficiency of cobalt, manganese, nickel and lithium by $[\text{P}_{888}][\text{Oleate}]$, using an IL:feed ratio of 1:1.

APPENDIX 3.D

SCREENING AND SCOPING TESTS FOR METAL REGENERATION

The screening experiments focusing on the regeneration of ionic liquid were initially performed with different types of sodium/ammonium salt solutions to find the most suitable regeneration solution(s) for the selective recovery of metal ions from the loaded [P₈₈₈][oleate] without affecting the functionality of the used IL. In this set of experiments a feed solution has been used without pH adjustment (i.e, pH =5), therefore IL has been loaded with Co, Ni and Mn while Li remains in the raffinate.

Table 3.D.1: List of regeneration solutions for screening and scoping tests of metal regeneration.

Regeneration Solution ID	Ammonium/ Sodium salts								
	Na ₂ CO ₃	NaNO ₃	Na ₃ PO ₄	Na ₂ SO ₄	NH ₄ OH	NH ₄ Cl	(NH ₄) ₂ CO ₃	(NH ₄) ₂ SO ₄	NH ₄ HCO ₃
RS-1	-	-	-	-	1.0 M	-	1.1 M	0.9 M	-
RS-2	-	-	-	-	1.0 M	-	1.2 M	1.0 M	-
RS-3	-	-	-	-	1.0 M	-	1.3 M	1.1 M	-
RS-4	-	-	-	-	1.0 M	-	1.4 M	1.2 M	-
RS-5	-	-	-	-	1.0 M	-	1.0 M	0.8 M	-
RS-6	-	-	-	-	-	-	1.0 M	1.0 M	-
RS-7	1.0 M	-	-	-	-	2.0 M	-	-	-
RS-8	1.0 M	-	-	-	-	-	-	-	-
RS-9	-	1.0 M	-	-	-	-	-	-	-
RS-10	-	-	0.5 M	-	-	-	-	-	-
RS-11	-	-	-	1.0 M	-	-	-	-	-
RS-12	-	-	-	-	-	0.5 M	-	-	-
RS-13	-	-	-	-	-	1.0 M	-	-	-
RS-14	-	-	-	-	-	2.0 M	-	-	-
RS-15	-	-	-	-	-	-	0.5 M	-	-
RS-16	-	-	-	-	-	-	1.0 M	-	-
RS-17	-	-	-	-	-	-	-	-	0.5 M
RS-18	-	-	-	-	-	-	-	-	1.0 M
RS-19	-	-	-	-	-	-	-	-	2.0 M

SINGLE SALT SOLUTION

For the first set of regeneration experiments 1 M of sodium sulphate, sodium carbonate, sodium bicarbonate, sodium nitrate and 0.5 M sodium phosphate have been used. The regeneration efficiency of cobalt, manganese and nickel using sodium nitrate is negligible while it is around 30-40 % using sodium sulphate in the form of aqueous metal sulphate for both first and second regeneration cycle. Sodium carbonate and sodium phosphate show higher regeneration efficiency above 95 % in which all loaded metals were precipitated. Sodium bicarbonate results in the precipitation of metal ions with lower regeneration

efficiency fluctuating between 84% and 98% based on the regenerated metal and cycle. All above mentioned sodium salts show poor selectivity as shown in Figure 3.D.1.

Figure 3.D.1: regeneration efficiency with 1 M of sodium carbonate, sodium bicarbonate, sodium sulphate and 0.5 M sodium phosphate in aqueous phase. Part dissolved in regeneration raffinate and part as precipitate.

The second set of regeneration experiments was done using different concentrations of ammonium chloride, ammonium carbonate and ammonium bicarbonate. Regeneration with ammonium chloride at 0.5M shows the highest selectivity for nickel against cobalt but the regeneration efficiency of nickel in one step process is only 53% and cobalt regeneration efficiency is 6%. Increasing the concentration of ammonium chloride up to 2M increases nickel regeneration efficiency up to 86% but cobalt regeneration increases as well, which consequently reduces the selectivity for nickel against cobalt. The percentage of manganese in the regeneration raffinate remains very low giving high separation of nickel from manganese at 2M NH_4Cl (Figure 3.D.2).

Regeneration using ammonium bicarbonate and ammonium carbonate (Figure 3.D.2) show similar separation behaviour as ammonium chloride where nickel selectivity against cobalt remains low regardless the concentration of ammonium salts. An increase in ammonium salt concentration increases the total recovery of all metals (in the regeneration raffinate and precipitate) and at the same time reduces the precipitation of nickel and cobalt (more nickel and cobalt are present in the regeneration raffinate).

This can be explained by the increase in ammonium ions which in it turn increases the formation of stable cobalt and nickel ammine complexes. On the other hand manganese does not form stable soluble complex in excess ammonia [54].

The use of ammonium salt solutions for metal recovery provides higher selectivity than sodium salt solutions. However, the selectivity needs to be improved via, for instance, multi-salt regeneration solution to selectively recover cobalt and manganese [55]. Since it is found that decreasing the pH before extraction to -0.9 is the most opportune manner to separate nickel and lithium from cobalt and manganese.

Figure 3.D.2: Regeneration using different concentrations of (a) ammonium chloride (b) ammonium carbonate and (b) ammonium bicarbonate. Part dissolved in regeneration raffinate and part as solid precipitate.

MULTI-SALT SOLUTION

As Figures 3.D.1 and 3.D.2 show, irrespective the identity of the single salt used, regeneration efficiencies were relatively low and metal separation far from complete. Therefore, the effectiveness of combinations of salts in terms of regeneration and separation were investigated next. Different combinations of Na_2CO_3 , NaNO_3 , Na_3PO_4 , Na_2SO_4 , NH_4OH , NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_2\text{SO}_4$ and NH_4HCO_3 were used. A distinction was

made between the relative amount of the recovered metal appearing in solution or as precipitate. Different combinations of ammonium and sodium salts were used to examine the possibilities for selective recovery of cobalt against manganese. First, applying a solution of 2 M ammonium chloride and 1 M sodium carbonate resulted in regeneration efficiency of 64% and 6% after four stages for cobalt and manganese respectively in which both metal ions remain in regeneration solution (Table 3.D.2). Secondly, using a solution of 1 M ammonium carbonate and 0.8 M ammonium sulphate shows better regeneration of cobalt and manganese with regeneration efficiency of 97% and 67% respectively in two regeneration steps. However, the selectivity is still poor. Then, the addition of 1 M ammonium hydroxide to the previous regeneration solution induced a good regeneration efficiency of cobalt around 97 % and manganese around 74 % within one step as well as good separation of cobalt and manganese as cobalt forms a stable complex with ammonia and stays in the regeneration solution while manganese precipitates as carbonate (Table 3.D.3). The replacement of ammonium sulphate by ammonium sulphite in the regeneration solution resulting in the ideal composition for the separation and precipitation method of manganese proposed by Kono et al., reduced the regeneration efficiency and changed the appearance of $[P_{888}][Oleate]$ [55]. Therefore, the optimal combination of ammonium salts consists of ammonium hydroxide, ammonium carbonate and ammonium sulphate. Then various experiments were performed to fine tune the ideal concentration of each salt as illustrated in Figure 3.4. RS-2 has been selected since it achieves the highest regeneration efficiency as well as the best separation between cobalt and manganese. Two steps regeneration was necessary to recovery >90% of manganese while almost 100% of cobalt was recovered in single step.

With the best regeneration solution defined as the one resulting in complete separation of cobalt and manganese (i.e., 100% of either one in solution and 100% of the other one as precipitate), the optimal regeneration solution should contain ammonium hydroxide, ammonium carbonate and ammonium sulphate. Taking into account the relative amounts of each, solution RS-2 was selected to be the best option.

Table 3.D.2: Regeneration efficiency of Co, Mn and Ni using 2 M NH_4Cl and 1 M Na_2CO_3 as regeneration solution in four stages.

Stage	$\eta_{R,i}$ in raffinate		
	Co	Mn	Ni
1	5.6	1.0	3.6
2	19.1	0.6	1.4
3	35.3	1.8	1.3
4	4.3	2.4	-

Table 3.D.3: Regeneration efficiency of Co, Mn and Ni using 1 M $(\text{NH}_4)_2\text{CO}_3$, 1 M NH_4OH and 0.8 M $(\text{NH}_4)_2\text{SO}_4$.

Metal	$\eta_{R,i}$			
	Raffinate		Precipitate	
	Co	Mn	Co	Mn
Cycle 1	96.8	2.9	5.4	70.4
Cycle 2	99.4	20.1	0.3	40.9

Remark: High concentration of Mn in the raffinate from second cycle was due to direct analysis after regeneration. In fact, the raffinate needs to be left to stand for at least one day to allow complete precipitation of Mn.

APPENDIX 3.E

Figure 3.E.1: FTIR spectra for NiCO₃ precipitate.

Figure 3.E.2: FTIR spectra for MnCO₃ precipitate.

APPENDIX 3.F

Table 3.F.1: Economic potential analysis (EP0) has been performed for 1 ton spent lithium ion battery leached in 10 and 50 m³ 4-8 M HCl.

EP0 analysis for metal recovery from spent LIB		
Feed solution		
Metal	wt. % [52]	1 ton Feed [kg]
Co	14.88	148.8
Ni	21.87	218.7
Mn	16.96	169.6
Li	5.75	57.5
Leaching and neutralization cost		
32 wt.% HCl price [\$ /ton]	150*	
NaOH [\$ /ton], pearls	400*	
Total cost (k\$/ton spent LIB)		
Acid Concentration [M]	Leachate volume 50 m ³	Leachate volume 10 m ³
4	7.1	1.8
5	8.7	2.1
6	10.4	2.4
8	13.7	3.1
Income from cobalt recovered per ton spent LIB		
Cobalt price [\$ /kg]	35	
Sales of Co [k\$/ton spent LIB]	5.2	

*Prices according to Alibaba.com

Nomenclature		
Symbols	Description	Unit
$C_{f,o}$	Co concentration in the feed	g/L
$C_{r,i}$	Co concentration in the raffinate - cycle i	g/L
$C_{LeIL,i}$	Co concentration in the lean IL - cycle i	g/L
$C_{LeIL,i-1}$	Co concentration in the lean IL - cycle i-1	g/L
$V_{f,i}$	Volume of the feed - cycle i	L
$V_{IL,i}$	volume of IL phase – cycle i	L
Greek letters		
$\eta_{E,i}$	Extraction efficiency for cycle i	%
$\eta_{R,i}$	Regeneration efficiency for cycle i	%
Subscripts		
aq	Aqueous phase	
IL	Ionic liquid	
HIL	Hydrophobic ionic liquid	
LLX	Liquid- liquid extraction	

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CHAPTER 4

THERMODYNAMICS AND PHYSICAL PROPERTIES OF AN IONIC LIQUID-BASED METAL EXTRACTION PROCESS

The important thing is to never stop questioning

Albert Einstein

ABSTRACT

A systematic approach is used to investigate the extraction mechanism of metal ions from an aqueous solution using an IL. In this chapter a LLX process is discussed in the context of the extraction of cobalt by the IL $[P_{888}][Oleate]$ as an example of transition metal extraction. Activity and chemical (FTIR) analyses indicate that Co complexes in the IL phase. Three different models are evaluated, all different with respect to the Co species that complexes with the IL. This thermodynamic analysis points towards the presence of $CoCl_2$ within the IL as a metal-IL complex. Furthermore, the complexation reaction between the Co and the IL is an endothermic entropy driven reaction. Finally, the influence of the feed composition on Co extraction is investigated including the effect of the nature of the accompanying anion as well as the salting out agent cation. The higher Co extraction from a NO_3 medium is due to the stronger interaction between $Co(NO_3)_2$ and the IL, reflected by a higher equilibrium constant of $Co(NO_3)_2$ compared to $CoCl_2$, both fitted for a complexation reaction with a Co:IL ratio of 1:2, performed at room temperature. Additionally, the observed difference in Co uptake in the presence of salting-out agent (NaCl, KCl and NH_4Cl) can be explained in terms of the hydration energy of the salting out cation.

4.1 INTRODUCTION

Since the year 2000, the use of ionic liquids (ILs) as an extractant/solvent for metal separation and purification has been intensively investigated [1, 2]. The main incentive for the use of ILs in metal extraction as alternative for conventional volatile organic solvents (VOCs) was their green character [3-6]. However, as already indicated, their negligible vapor pressure is not sufficient to classify ILs as 'green solvents', due to their solubility in aqueous media, as this may lead to water pollution which threatens the aquatic environment [7, 8]. Regardless, ILs are still considered by metallurgists as a potential alternative due to their high selectivity and flexibility of independently changing either the cation or anion that can be fine-tuned to a specific separation process [8, 9].

The majority of the reported studies tends to focus on specific applications of ILs in metal extraction and separation [2]. These are important efforts, however many fundamental aspects related to the chemistry, physics and thermodynamics of the IL remain poorly understood [2]. In particular, the unique solvent environment offered by ILs creates mechanisms for metal ion transfer to IL phases that have no analogues in molecular liquids. Unlike molecular solvents, in which the metal is extracted as a neutral hydrophobic metal-ligand complex, ILs are also able to accommodate charged metal complexes or ions [10]. Hence, the speciation of metal ions is completely different than in traditional solvents. This means that the process involves concomitant transfer of ions either from the IL to the aqueous phase (ion exchange) or from the aqueous to IL phase (ion pair extraction) to maintain a charge balance between the phases. Furthermore, the hydrophobic nature of ILs allows complexes to be formed which are substantially different from those observed in water.

Recently, Lommelen et al., proposed a model based on coordination chemistry for metal extraction from chloride media using a quaternary ammonium salt IL (methyltrioctylammonium chloride) [11]. That particular model relies on the hypothesis that the metal species with the lowest charge density and thus lowest hydration level is extracted preferentially. Additionally, the author envisions the extraction of metal ions from chloride media as a series of elementary thermodynamic steps: (1) the formation of the partially hydrated neutral metal salts (e.g., MCl_2), (2) the extraction of the metal salt into the organic phase, and (3) the complexation of the metal salt with the organic phase via replacing the hydrated water molecules of the neutral metal salt by the anion available in the organic phase to form negatively charged metal complexes that electrostatically interact with the organic cation [11, 12].

The extraction of metal ions is significantly influenced by the composition of the aqueous solution, including the nature of the accompanying anion and the addition of a salting

out agent [6, 13]. In 1888, Hofmeister developed a series that ranks ions according to their effect on the solubility of proteins in the aqueous solution [14]. Salting out agents reduces the solubility of proteins, while salting in agents increase the solubility of proteins. Prior studies show that the Hofmeister series is applicable for metal extraction as well [11, 15, 16]. However, the underlying principles were not completely elucidated [16]. Additionally, some studies relate the effect of adding monovalent salting out agents to the increase in the anion concentration, when the anion of the salting out agent is the same as that of the extracted species, which enhances the formation of metal-halide salts [6, 17]. A recent study links the effect of adding these salts to the principle of ion hydration rather than influencing metal ion speciation [13]. This proposed that the salting out cation with largest hydration energy, creates an environment that has the lowest amount of free water molecules available within the aqueous phase, and as a result provides a lower hydration level for the transition metal ion [13].

In this Chapter, the extraction mechanism of Co from chloride (Cl) and nitrate (NO₃) aqueous media using [P₈₈₈][Oleate] has been evaluated from a thermodynamic point of view. Thermodynamic analysis involves studying the extraction isotherm, evaluating the thermodynamic parameters (equilibrium constant, Gibbs free energy, enthalpy and entropy of metal-IL complexation reaction), as well as understanding the complexation reaction taking place in this liquid-liquid extraction (LLX) process. This analysis begins by describing the possible Co speciation, and then presents and discusses all possible mechanisms for ion transfer with an emphasis on understanding their thermodynamic parameters. This is followed by a discussion of how the extraction process is influenced by the nature of the accompanying anion and the addition of salting out agents.

4.2 EXPERIMENTAL

4.2.1 MATERIALS AND ANALYSIS

Tetraoctylphosphonium bromide (> 95 %) was purchased from IoLiTec; sodium chloride (NaCl), ammonium chloride (NH₄Cl), potassium chloride (KCl), and nitric acid (HNO₃) (69 %) from VWR Chemicals; oleic acid (90 %), perchloric acid (HClO₄) (70 %), cobalt (II) chloride hexahydrate (CoCl₂ × 6 H₂O) (98 %) and cobalt (II) nitrate hexahydrate (Co(NO₃)₂ × 6 H₂O) (98 %) from Alfa Aesar. MilliQ water (≥18 MΩ.cm) was obtained from a Millipore Milli-Q® Biocel, which uses a Qgrade® column. All chemicals were used as received, without any further purification. Tetraoctylphosphonium oleate [P₈₈₈][Oleate] was synthesized according to the procedure described in Chapter 3 [18].

The aqueous phases after each extraction process were analysed by a Metrohm IC Compact 761 ion chromatograph (detection range: 0.1-80 mg/L) and a Perkin Almer Optima 5300

DV inductive coupled plasma optical emission spectrometry (ICP-OES) (detection range: 0.025 - 10 mg/L). The organic phase was digested using a Milestone Ethos Easy microwave digester and analysed using the same instruments as applied for the aqueous phase. The pH and the conductivity of the aqueous and the organic phase were measured using a Mettler Toledo pH-meter with an accuracy of ± 0.002 . The temperature change was monitored using Universal Data Manager Ecograph T RSG35. Ultraviolet-visible spectroscopy (UV-VIS) was used to identify the form of the Co complex presents in the aqueous and the organic phase (IL). Fourier transform infrared spectroscopy (FTIR) is use to identify the changes in the change in the chemical structure of the fresh and loaded IL.

4.2.2 EXTRACTION EXPERIMENTS

Batch extraction experiments were performed using feed solutions containing 1.7×10^{-3} -1 M Co (0.1-60 g/L) from its corresponding Cl or NO_3 salts without pH adjustment. NaCl has been added to the feed solution of all experiments with equal concentration of Na to Co on mass basis unless stated otherwise. In each experiment, 5 ml aqueous phases mixed with 5 ml water-saturated $[\text{P}_{888}][\text{Oleate}]$ (around 10 wt. % water) for 10 min at 40 rpm and centrifuged (3750 rpm; 10 min, 22°C) in an Allegra X-12R Centrifuge of Beckman Coulter. In section 4.3.2 equilibrium experiments were also performed using diluted fresh and regenerated solvent which is composed of extractant (IL), diluent (n-dodecane) in a 1:2 weight ratio and 5 wt.% IPA. The extraction of Na from either chloride or nitrate aqueous solution was studied using the same procedure as applied for Co extraction where feed solutions contain 4.3×10^{-3} -1 M Na (0.1-23 g/L). At 50 and 80 °C experiments were performed using feed solutions containing 1.7×10^{-3} -0.85 M Co (0.1-50 g/L) and equal concentration of Na in g/L. NaCl, KCl and NH_4Cl are used as salting-out reagent to improve the extraction efficiency. To measure the temperature change during LLX, a new set of experiments were performed in an isolated Y shaped tube. This Y shaped tube was used to allow monitoring the temperature change during the first minutes of the extraction. Initially the aqueous and the organic phase were separately added to different compartments and then mixed for 30 min.

4.3 RESULTS AND DISCUSSION

The Co extraction behaviour of the IL is affected by various parameters. These include temperature and the feed composition such as the nature of the accompanying anion and the presence of other, non-extracted salts (i.e., the salting out agent). To study the effect of the feed composition in more detail, extraction experiments were performed in solutions either containing solely CoCl_2 , $\text{Co}(\text{NO}_3)_2$, NaCl or NaNO_3 , or, alternatively, a combination of these salts. It should be emphasized that we restrict this analysis to the first cycle

during which Co is taken up with the accompanying anion in a fixed 1:2 stoichiometry (see Chapter 2).

4.3.1 TEMPERATURE EFFECT AND EXTRACTION MECHANISM (FIRST CYCLE)

To evaluate the extraction capacity and thermodynamic parameters of the system under investigation, the extraction isotherms of Co with $[P_{888}][\text{Oleate}]$ were investigated at different temperatures (i.e. 295, 323, 353K). These experiments were performed using fresh $[P_{888}][\text{Oleate}]$ as the solvent, where the extraction mechanism in the first cycle is based on ion pair as discussed in an earlier study by Othman et al., (see Chapter 2) [18]. Figure 4.1 shows the isotherms with the equilibrium Co concentrations in both the IL and the aqueous phase at three different temperatures. It is clearly shown that Co uptake increases with increasing temperature, implying that the extraction process of Co by $[P_{888}][\text{Oleate}]$ is endothermic in nature. The overall endothermicity of the extraction might be caused by an endothermic reaction of the Co with the IL phase. In fact, when comparing the FTIR spectra (Figure 4.A.1) of the loaded IL with that of fresh IL, a difference is indeed observed. This indicates that an interaction (complexation reaction) between the extracted Co and the IL does take place. The main difference between the two spectra is the absence of the asymmetric C=O stretch in the spectrum of the loaded IL. This further suggests that the coordination takes place through the carboxyl group of the oleate [19].

Another way to look at the complexation reaction between the IL and Co is to calculate the free Co activity in the IL after pre-loading the IL with different amounts of Co. As shown in Figure 4.2 and further discussed in Appendix 4.B, at any given amount of dissolved Co in the IL, the calculated Co activity decreases with increasing temperature. The activity of free Co in the IL is calculated based on the equilibrium condition in which the free Co activity in the raffinate equals the free Co activity in the IL. We assume that in both phases all Co is presents as Co^{2+} and that temperature hardly affects the activity of free Co in the IL as it does in the aqueous phase (see Figure 4.B.1, Appendix 4.B). This assumption seems reasonable since the IL contains water in which the free Co can be present.

Based on these assumptions, this analysis also points in the direction of an endothermic complexation reaction. Working this out in more detail with an example: At a concentration of ~ 0.65 M total Co (free and complexed) in the IL the activity of free Co in the IL is considerably lower at higher temperature. Because we assumed that the activity of free Co in the IL is hardly affected by the temperature, this means that at higher temperature the concentration of free Co in the IL is lower. As we are comparing experiments at constant total Co concentration in the IL phase, this hint towards that at higher temperature a larger part of the Co is stored in a complex by a chemical reaction. The trend of more stored Co in a complex at higher temperature can be explained by an endothermic reaction for which the equilibrium conversion increases with temperature. Additional support for this

conclusion comes from the reduction in the measured electric conductivity of loaded IL, as discussed in Appendix 4.C.

Figure 4.1: Extraction isotherm of Co using fresh IL $[P_{888}][Oleate]$ during the first cycle. Plotted values represent equilibrium concentrations in the raffinate and in the IL. Feed solution containing equal concentration of Co and Na on mass basis from their corresponding chloride salts.

Figure 4.2: The effect of temperature on the calculated Co activity in the aqueous phase (equal to the free Co activity in the IL) at different dissolved Co concentrations in the IL. Note: the reduction in the activity is due to a change in the amount of free Co in the IL and not due to temperature effect as discussed above and in Appendix 4.B.

The thermodynamic parameters were first evaluated based on the chemical reaction stoichiometry demonstrated by (Eq. 4.1) which was proposed by Parmentier et al., in their study of a similar system [20]. Parmentier et al., described the mechanism of Co extraction

by tetraoctylammonium oleate via the formation of a metal carboxylate complex that is then transferred to the IL phase, together with the necessary counter-anions that keep the charges balanced. The overbars represent the organic phase.

Based on the equation above, if three IL molecules are involved in the extraction of one Co, this will reflect a maximum capacity of 0.35 mol of Co per 1.06 mol of IL. However, the experimental data displayed in Figure 4.1 show a continuous increase in Co uptake with increasing equilibrium Co concentration in the aqueous phase far beyond the theoretical level of 0.35 mol of Co per 1.06 mol of IL. For instance, at a Co raffinate concentration of approximately 0.1 M, the Co concentration in the IL is > 0.4 M, irrespective the temperature. This could indicate that the extraction mechanism based on the assumption that all the extracted Co is complexed with the IL is not valid for the studied system, and that part of the Co remains in its unbound, free form. Alternatively, the stoichiometry Co:IL may be less than the assumed 1:3. Using a feed solution containing around 1 M Co and an equal concentration of Na on mass base operated at room temperature will result in a Co uptake of 0.67 mol per mol IL, reflecting that the stoichiometry of 1:2 is also not applicable.

In the next section the model of Parmentier et al., is adapted, first, by assuming that Co in the IL can be present in two forms, complexed with the IL and free, and, secondly, by exploring different Co:IL stoichiometries. The link between the two bulk phases is the partitioning coefficient m representing the ratio of a particular Co species in the IL and aqueous phase. Each model differs in respect to the assumed present Co species that complexes with the IL, be that Co^{2+} , CoCl^{+} or CoCl_2 . Also note that for reasons of brevity any possible hydration water of Co and Co-IL complex in both the water and the IL phase is left out the reactions because it has no effect on the final result.

MODEL A

This model assumes that Co is extracted as free ion. To maintain electroneutrality, the extraction of Co is accompanied by the extraction of two Cl ions. The first step comprises crossing the interface separating the aqueous and IL phase. Next, Co and Cl diffuse away from the interface into the bulk of the IL phase where the metal-IL complexation takes place. At equilibrium the interface concentrations will be equal to the bulk concentrations. The only difference with the model of Parmentier et al., thus is that Co can reside in two forms in the IL, either bound to the IL or free.

a. Model A.1:3

The corresponding equilibrium constant and partitioning coefficient (m) are defined by Eq. (4.3) and (4.4), respectively. The total Co in the IL phase includes both the free and complexed Co: $([Co^{2+}]_{Total} = [Co^{2+}] + [P_{8888}[Co(Oleate)_3]])$. Likewise, the total IL includes both the free and the complexed IL $([P_{8888}[Oleate]_{Total} = [P_{8888}[Oleate] + 3 [P_{8888}[Co(Oleate)_3]])$.

$$K_{eq} = \frac{[P_{8888}[Co(Oleate)_3]] [P_{8888}[Cl]]^2}{[Co^{2+}] [Cl^-]^2 [P_{8888}[Oleate]]^3} \quad (4.3)$$

$$m = \frac{[Co^{2+}]}{[Co_{aq}^{2+}]_{Total}} \quad (4.4)$$

Eq. (4.3) can be further simplified due to the ion-pair extraction mechanism. Therefore, the chloride concentration $[Cl^-]$ in the IL phase is equivalent to two times the $[Co^{2+}]$ concentration in the IL phase ($2[Co^{2+}] = [Cl^-]$) and the concentration of chloride-IL complex $[P_{8888}[Cl]]$ is equal to two times the concentration of complex $[P_{8888}[Co(Oleate)_3]]$ ($2[P_{8888}[Co(Oleate)_3]] = [P_{8888}[Cl]]$). And writing $[Co^{2+}]$ in terms of m and $[Co_{aq}^{2+}]_{Total}$ Eq. (4.3) then simplifies to:

$$K_{eq} = \frac{[P_{8888}[Co(Oleate)_3]]^3}{m^3 [Co_{aq}^{2+}]_{Total}^3 [P_{8888}[Oleate]]^3} \quad (4.5)$$

The value of the equilibrium constant K_{eq} and partitioning coefficient m are obtained by fitting the experimental data of Figure 4.1 to Eq. (4.5), at three different temperatures (Table 4.1). The fitting procedure minimizes the value of the mean square error (MSE) between the experimental and fitted total Co uptake. Figure 4.3 panel A.1:3 compares the measured Co uptake with the modelled Co uptake given the fitted values of K_{eq} and m at different temperatures. It is clear that the experimental data is well-fitted using this model with a relative error of less than 30% for most of the data points.

Figure 4.3: Parity plots of Co uptake comparing the experimental data sets at different temperature (i.e., 295, 323 and 353 K) with the results of **model A**, using a Co: IL stoichiometric ratio of either 1:3 (left), 1:2 (middle) or 1:1 (right).

Once the values of K_{eq} has been obtained, thermodynamic parameters such as the changes in the free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) associated with the extraction of Co by IL were evaluated using the Van 't Hoff equation, with the assumption that both the enthalpy and entropy changes are constant in the temperature range applied:

$$\Delta G^\circ = -RT \ln K_{eq} \quad (4.6)$$

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4.7)$$

The plot of $\ln K_{eq}$ as function of $1/T$, with K_{eq} (and m) obtained from the fits of the isotherm data shown in Figure 4.1 and corresponding to Eq. (4.7), results in a straight line with a slope ($-\Delta H^\circ/R$) and an intercept ($\Delta S^\circ/R$) (see Figure 4.4 panel A.1:3). This renders a positive ΔH° of 65 kJ/mol, corresponding to an adiabatic temperature change of -12 K during the extraction experiment (i.e., loading IL with 0.34 M Co) assuming that the measured temperature effect is dominated by the complexation reaction between the extracted Co and the IL. However, no noticeable temperature change was observed during the extraction of Co. This may indicate that the extraction mechanism of Co by $[P_{888}][Oleate]$ follows a different stoichiometry or mechanism than proposed by Parmentier et al., [20].

Figure 4.4: Effect of temperature on the extraction equilibrium constants of Co obtained using **model A** with Co: IL ratio's of 1:3 (left), 1:2 (middle) and 1:1 (right). Feed solutions contain a Co concentration of 0.02- 1 M and an equal concentration of Na in (g/L), present as Cl salt.

Therefore Eq. (4.2) (Model A. 1:3) was re-evaluated using a different stoichiometry (i.e., 1:2 or 1:1 for Co:IL) as presented in Eqs. (4.8) and (4.9) respectively:

b. Model A.1:2

$$K_{\text{eq}} = \frac{[\overline{\text{Co}(\text{Oleate})_2}][[\text{P}_{888}][\text{Cl}]]^2}{[\overline{\text{Co}^{2+}}][\overline{\text{Cl}^-}]^2[\text{P}_{888}][\text{Oleate}]^2} \quad (4.9)$$

In analogy to Eq. (4.5), the simplified expression is:

$$K_{\text{eq}} = \frac{[\overline{\text{Co}(\text{Oleate})_2}]^3}{m^3 [\text{Co}_{\text{aq}}^{2+}]^3 [\text{P}_{888}][\text{Oleate}]^2} \quad (4.10)$$

c. Model A. 1:1

$$K_{\text{eq}} = \frac{[\overline{\text{CoCl}(\text{Oleate})}][[\text{P}_{888}][\text{Cl}]]}{[\overline{\text{Co}^{2+}}][\overline{\text{Cl}^-}]^2[\text{P}_{888}][\text{Oleate}]} \quad (4.12)$$

In analogy to Eq. (4.5), the simplified expression is:

$$K_{eq} = \frac{[\overline{\text{CoCl(Oleate)}}]^2}{4 \text{ m}^3 [\text{Co}_{aq}^{2+}]^3 [\text{P}_{888}][\text{Oleate}]} \quad (4.13)$$

Figure 4.3 panels A.1:2 and A.1:1 show that changing the reaction stoichiometry reduces the fitting ability compared with model A.1:3, notably in the case of a 1:1 stoichiometry. The plot of $\ln K_{eq}$ versus $1/T$ for a stoichiometry of either 1:2 or 1:1, as presented in Figure 4.4 panels A.1:2 and A.1:1, result in a positive ΔH° of 43 kJ/mol and 222 kJ/mol, respectively. This means that loading the IL with 0.34 M Co would correspond to an adiabatic temperature change of -8 and -40 K for the 1:2 and 1:1 stoichiometry, respectively, as shown in Table 4.1.

Since the change of the reaction stoichiometry reduces the fitting ability of the data and shows no improvement in terms of the adiabatic temperature change during the LLX process, the next section evaluates different complexation mechanisms.

It has been reported in the literature that quaternary phosphonium or ammonium based ILs behave as basic extractants where the anionic part reacts with metal salts to form negatively charged metal complexes that electrostatically interact with the cationic part of the IL [13, 17, 21-24]. Translated to our system, oleate reacts with the Co salt to create a negatively charged metal carboxylic complexes that electrostatically interact with the cationic part of the IL providing a metal-IL complex in the form of $([\text{P}_{888}][\text{Oleate}])_n \text{CoCl}_2$. Lommelen et al., hypothesized that the metal species in the aqueous phase with the lowest charge density and lowest hydration state are most efficiently extracted [11]. The reason would be that metal species with higher charge densities are relatively more stabilized in the aqueous phase compared to metal species with low charge densities and uptake by the IL requires a (partly) dehydration of the metal ion species [11]. Based on reported literature, there can be up to five different species of Co be present in aqueous chloride media depending on the Cl concentration (i.e., CoCl_x^{2-x} with $0 \leq x \leq 4$), nevertheless many studies on the speciation of Co in aqueous media are inconsistent [11]. According to Zeltmann et al., there are three species that exist in aqueous media with chloride concentration up to 5 M; two octahedral species Co^{2+} and CoCl^+ and one tetrahedral CoCl_2 [25]. The concentration of different Co species varies depending on Cl concentration in the aqueous phase. In the present study, we explore the extraction of Co as either Co^{2+} , CoCl^+ or CoCl_2 since the Cl concentration ranges from 0.006 M to 4.6 M. Model A, already discussed, assumes that free Co in the IL is present as Co^{2+} . Models B and C, discussed next, assume that free Co in the IL is present as either CoCl^+ or CoCl_2 . This means that this particular Co species is extracted either as it is present in the aqueous phase or formed instantaneously at the interface within the aqueous phase before entering the IL. All three

models also assume that the particular Co species forms a metal complex with the IL, with a Co:IL stoichiometry of either 1:3, 1:2 or 1:1.

MODEL B

This model assumes that free Co in the IL is present as CoCl^+ . To maintain the electroneutrality, the extraction of CoCl^+ is accompanied by the extraction of one Cl ion. Then, the partitioning coefficient m , defined as the ratio of CoCl^+ concentration in the IL to the total Co concentration in the aqueous phase, is as expressed as the following:

$$m = \frac{[\text{CoCl}^+]}{[\text{Co}_{\text{aq}}^{2+}]_{\text{Total}}} \quad (4.14)$$

Then the extracted CoCl^+ and Cl react with the IL according to the following equation:

$$K_{\text{eq}} = \frac{([\text{P}_{888}][\text{Oleate}])_n \text{CoCl}_2}{[\text{CoCl}^+][\text{Cl}^-][\text{P}_{888}][\text{Oleate}]^n} \quad (4.16)$$

Eq. (4.16) can be rewritten in terms of m and when the constraints discussed about the simplification of Eq. (4.3) are applied:

$$K_{\text{eq}} = \frac{([\text{P}_{888}][\text{Oleate}])_n \text{CoCl}_2}{m^2 [\text{Co}_{\text{aq}}^{2+}]^2 [\text{P}_{888}][\text{Oleate}]^n} \quad (4.17)$$

Model B is evaluated for three different $\text{CoCl}^+:\text{IL}$ ratios 1:3, 1:2 and 1:1 where n in Eq. (4.15) equals 3, 2 or 1 respectively. Figure 4.5 panel B.1:3 shows that model B with a ratio of 1:3 can predict the experimental data very well. However, plotting $\ln K_{\text{eq}}$ versus $1/T$ for this model (Figure 4.6 panel B.1:3) with the K_{eq} (and m) obtained from fitting the isotherm data as shown in Figure 4.1 to Eq. (4.17) provides a positive ΔH° of 47 kJ/mol, reflecting an adiabatic temperature change of -9 K for loading IL with 0.34 M Co (Table 4.1). This value is still high compared to the neglectable temperature change actually measured ($\Delta T < -1$ K). Figure 4.5 panels B.1:2 and B.1:1 show that model B with ratios of 1:2 and 1:1 cannot predict Co uptake at low concentration especially below 0.2 M and below 0.4 M, respectively.

Figure 4.5: Parity plots of Co uptake comparing the experimental data sets at different temperature (i.e., 295, 323 and 353 K) with the results of **model B** with different CoCl⁺ : IL ratios 1:3 (left), 1:2 (middle) or 1:1 (right).

Figure 4.6: Effect of temperature on the extraction equilibrium constants of Co obtained using **model B** with CoCl⁺ : IL ratios 1:3 (left), 1:2 (middle) or 1:1 (right). Feed solutions contain Co concentration 0.02- 1 M and equal concentration of Na in g/L from their corresponding Cl salts.

MODEL C

This model assumes that free Co in the IL is present as neutral CoCl₂. Then, the partitioning coefficient m , defined as the ratio of CoCl₂ concentration in the IL to the total Co concentration in the aqueous phase, is as expressed as the following:

$$m = \frac{[\overline{\text{CoCl}_2}]}{[\text{Co}_{\text{aq}}^{2+}]_{\text{Total}}} \quad (4.18)$$

Then the extracted CoCl_2 reacts with the IL according the following reaction equation:

$$K_{\text{eq}} = \frac{[(\overline{\text{P}_{888}}][\overline{\text{Oleate}}])_n \overline{\text{CoCl}_2}]}{[\overline{\text{CoCl}_2}] [\overline{\text{P}_{888}}][\overline{\text{Oleate}}]^n} \quad (4.20)$$

Eq. (4.20) can be rewritten in terms of m and considering the same constraints discussed regarding the simplification of Eq. (4.3):

$$K_{\text{eq}} = \frac{[(\overline{\text{P}_{888}}][\overline{\text{Oleate}}])_n \overline{\text{CoCl}_2}]}{m [\text{Co}_{\text{aq}}^{2+}]_{\text{Total}} [\overline{\text{P}_{888}}][\overline{\text{Oleate}}]^n} \quad (4.21)$$

Model C is also evaluated for the three possible CoCl_2 :IL ratios 1:3, 1:2 and 1:1 where n in Eq. (4.19) equals 3, 2 or 1 respectively. Figure 4.7 and Table 4.1 show that model C with CoCl_2 :IL ratio of 1:2 can fit the experimental data very well. The obtained MSE for fitting model C.1:2 is as good as model A.1:3. However model C.1:2 results in a very modest temperature effect that is more congruent to the experimental temperature effect noticed. Figure 4.8 shows that the experimental extraction of Figure 4.1 can be described very well by the modelled isotherm, obtained by fitting the data to Eq. (4.21). Model C hypothesizes the existence of a neutral, partially hydrated complex (i.e., CoCl_2) at the interface. This neutral complex is then extracted to the IL phase and subsequently reacts with the anionic part (i.e., carboxyl group) of the IL according to Eq. (4.19). This hypothesis is consistent with a recent study which describes the metal extraction process as a series of elementary thermodynamic steps as discussed in section 4.1 [11]. Additionally, the experimental data from this study show that there is a shift in the UV-vis spectrum of Co from 500 nm in the aqueous phase to 578 nm in the IL phase (Figure 4.A.2). In the literature, it is reported that this characteristic wave length (around 578 nm) represents the presence of partially hydrated tetrahedral CoCl_2 salts (four-fold), where two of these folds or ligands can remain as hydrated water molecules or replaced by an organic reagent [26]. For example, the extraction of CoCl_2 by Acetone solution forms a $\text{CoCl}_2(\text{Acetone})_2$ complex which has the same characteristic shift as that obtained in the present study [27]. This is in line with the hypothesized extraction mechanism that Co is present within the metal- IL complex as CoCl_2 with the two originally present water molecules replaced by two IL oleates [26, 27].

Figure 4.7: Parity plots of Co uptake comparing the experimental data sets at different temperature (i.e., 295, 323 and 353 K) with the predictions of **model C** with different CoCl_2 : IL ratios 1:3 (left), 1:2 (middle) or 1:1 (right).

Figure 4.8: Extraction isotherm of Co with IL $[\text{P}_{888}][\text{Oleate}]$: data points are obtained experimentally and lines are model based (fitting the data according to Eq. (4.21) with CoCl_2 :IL of 1:2).

Figure 4.9 panel C.1:2 plots $\ln K_{\text{eq}}$ versus $1/T$ with K_{eq} and m obtained from the fits of the isotherm data shown in Figure 4.8 and corresponding to Eq. (4.21). Table 4.1 summarizes derived values of K_{eq} , m and the thermodynamic parameters ΔG° , ΔH° and ΔS° at three different temperatures. The obtained value of ΔH° of 22 kJ/mol translates into an ΔT of just -4 K (calculated for loading the IL with 0.34 M) as compared to the -12 K that was obtained previously (as well as being based on a different reaction mechanism). This result is in line with enthalpy changes calculated for Co complexes ($([\text{P}_{888\text{n}}]_2)_2\text{CoCl}_4$ and $([\text{P}_{666\text{n}}]_2)_2\text{CoCl}_4$

obtained with similar ILs [17]. These values are 28 kJ/mol, 17 kJ/mol, 33 kJ/mol and 24 kJ/mol using $[P_{8888}][Cl]$, $[P_{88814}][Cl]$, $[P_{88816}][Cl]$ and $[P_{66614}][Cl]$ respectively [17].

Figure 4.9: Effect of temperature on the extraction equilibrium constants of Co obtained using **model C** with $CoCl_2(H_2O)_2$; IL ratio 1:3, 1:2 and 1:1. Feed solutions contain Co concentration 0.02-1 M and equal concentration of Na in g/L from their corresponding Cl salts.

The process of the complex formation in the IL phase is endothermic, as evidenced by the positive ΔH° of the reaction. Irrespective of the temperature, the Gibbs free energy is negative, indicating that the reaction is spontaneous. The entropy of complexation is positive and given the positive ΔH° , indicating that the complexation process is entropy-driven. This may be due to (1) the release of water molecules from the primary coordination sphere of Co upon complexation with the IL-ligand or (2) the loss of an organized aggregation structure within the IL phase after the extraction of Co [17, 28, 29]. However, the amount of water in the IL, as measured by Karl-Fischer, did not increase upon the extraction of the partially hydrated $CoCl_2$. On the other hand, FTIR spectra showed a reduction in the intensity of the broad OH⁻ peak around 3450 cm^{-1} derived from H_2O (Figure 4.A.1). These two pieces of conflicting evidence can be reconciled taking into account that Karl-Fischer is too insensitive to detect the small release of water compared to the 10 wt.% of water already present in the IL.

In conclusion, based on the MSE values, the predicted adiabatic temperature rise (Table 4.1) as well as the $\ln K_{eq}$ versus $1/T$ plots, Model C, and specific for ratio Co:IL=1:2, seems most adequate in describing the data.

Table 4.1: Thermodynamic parameters of Co extraction by [P₈₈₈₈][Oleate]. Obtained K_{eq} and m values are the result of regression analysis of the different complexation models (A, B, C) discussed here, each for three different Co:IL stoichiometries.

Model	T [K]	K_{eq}	m	MSE	Kcc	Thermodynamic parameters			ΔT [K]
						ΔG° [kJ/mol]	ΔH° [kJ/mol]	ΔS° [J/mol]	
Model A (1:3)	295	$1.4 \times 10^{+3}$	1.1	1.3×10^{-4}	0.35	-17.8			
	323	$4.8 \times 10^{+4}$	1.4	5.9×10^{-4}	0.46	-28.9	65	285	-12
	353	$1.1 \times 10^{+5}$	2.3	6.5×10^{-4}	0.23	-34.0			
Model A (1:2)	295	$2.7 \times 10^{+3}$	0.5	4.9×10^{-4}	0.48	-19.4			
	323	$3.8 \times 10^{+4}$	0.5	2.1×10^{-3}	0.48	-28.3	43	213	-8
	353	$4.5 \times 10^{+4}$	1.1	1.7×10^{-3}	0.49	-31.4			
Model A (1:1)	295	$1.3 \times 10^{+2}$	0.4	1.2×10^{-2}	0.50	-12.0			
	323	$3.0 \times 10^{+4}$	0.1	1.6×10^{-2}	0.50	-27.7	222	786	-40
	353	$4.1 \times 10^{+8}$	0.01	2.1×10^{-2}	0.50	-58.2			
Model B (1:3)	295	$1.5 \times 10^{+3}$	1.2	3.8×10^{-4}	0.33	-17.9			
	323	$2.0 \times 10^{+4}$	1.4	7.3×10^{-4}	0.45	-26.6	47	224	-9
	353	$3.4 \times 10^{+4}$	2.4	7.7×10^{-4}	0.27	-30.6			
Model B (1:2)	295	$1.6 \times 10^{+3}$	0.5	1.3×10^{-3}	0.48	-18.0			
	323	$7.5 \times 10^{+3}$	0.6	3.3×10^{-3}	0.39	-24.0	26	151	-5
	353	$8.8 \times 10^{+3}$	1.1	2.8×10^{-3}	0.49	-26.6			
Model B (1:1)	295	$1.0 \times 10^{+3}$	0.2	1.3×10^{-2}	0.47	-16.9			
	323	$1.0 \times 10^{+0}$	2.5	1.7×10^{-2}	0.36	-0.0	112	407	-20
	353	$2.7 \times 10^{+6}$	0.01	2.1×10^{-2}	0.13	-43.4			
Model C (1:3)	295	$2.6 \times 10^{+1}$	1.4	5.5×10^{-4}	0.36	-8.0			
	323	$1.3 \times 10^{+2}$	1.7	8.2×10^{-5}	0.33	-13.0	29	127	-5
	353	$1.8 \times 10^{+2}$	2.7	1.1×10^{-3}	0.28	-15.2			
Model C (1:2)	295	$1.5 \times 10^{+1}$	0.9	2.1×10^{-4}	0.43	-6.7			
	323	$4.8 \times 10^{+1}$	1.0	6.5×10^{-4}	0.43	-10.4	22	99	-4
	353	$6.5 \times 10^{+1}$	1.6	4.6×10^{-4}	0.41	-12.3			

	295	$5.3 \times 10^{+2}$	0.01	1.1×10^{-3}	0.48	-15.4			
Model C (1:1)	323	$9.0 \times 10^{+2}$	0.01	4.7×10^{-3}	0.50	-18.3	18	113	-3
	353	$1.8 \times 10^{+3}$	0.01	5.0×10^{-3}	0.39	-22.0			

4.3.2 EXTRACTION MECHANISM FROM SECOND CYCLE ON

Model A, B and C discussed in section 4.3.1 were analysed using the experimental data obtained from the first cycle with the ion pair extraction mechanism. In an earlier study, it was found that the extraction mechanism shifts from ion pair in the first cycle to ion exchange in the subsequent cycles (see chapter 2) [18]. However, equilibrium experiments performed using IL diluted with n-dodecane and isopropyl alcohol show that the equilibrium isotherms of both fresh (pure and diluted IL) and regenerated diluted IL are almost identical (taking in to account the experimental error) as shown in Figure 4.10. This could be due to the fact that the Cl level in the IL is always the same (Co to Cl ratio is 1:2) regardless of the extraction mechanism. The level of Cl in the IL, extracted in the first cycle, remains unchanged in the subsequent cycles as a result of either one of the two following scenarios: (1) ion exchange between Co and Na (from the regeneration solution), or (2) salt exchange between CoCl_2 and NaCl. Therefore, it is expected that the conclusion regarding the complexation reaction between CoCl_2 and IL drawn based on the first cycle is applicable for the subsequent cycles as well.

Figure 4.10: Equilibrium curve for pure IL, fresh solvent and regenerated solvent (IL+n-dodecane in a 1:2 weight ratio with the addition of 5 wt.% isopropyl alcohol (IPA)). The Co concentration on the Y-axis is relative to the amount of IL present. Note, the amount of extracted metal is small and hardly change the volume of the IL.

4.3.3 EFFECT OF THE NATURE OF THE ACCOMPANYING ANION

The extraction behaviour of the IL is also affected by the nature of the accompanying anion. To study this effect in more detail, extraction experiments were performed in solutions either containing CoCl_2 or $\text{Co}(\text{NO}_3)_2$, the result is shown in Figure 4.11. The presence of NO_3 clearly enhances Co uptake. Prior to the formation of the Co salt and the subsequent complexation, the anion needs to be (partly) dehydrated. Despite the substantial difference in dehydration enthalpy of 381 kJ/mol for Cl and 314 kJ/mol for NO_3 , the different behaviour shown in Figure 4.11 is primarily based on a difference in complexation kinetics, reflected in the different shape of the initial part of both curves in Figure 4.11 [30]. Note that the second part of both curves run more or less parallel, indicating a similar distribution of both anion species over the two phases once the IL-Co complexation has been saturated. This was also confirmed by the m-value obtained from fitting the isotherm which was identical for both salts (will be discussed below)

Figure 4.11: Extraction isotherm of Co with IL $[\text{P}_{888}][\text{Oleate}]$ obtained from solutions either containing the chloride or nitrate-based Co salts at room temperature.

Another way to point to the minor effect of dehydration energy is to calculate the Boltzmann distribution of both anions over the two phases while assuming that prior to entering the IL both require total dehydration. Given a feed solution containing CoCl_2 , NaCl and NaNO_3 and based on the difference in the free energy of (complete) dehydration, the Boltzmann distribution predicts a $\left(P_{\text{NO}_3}^{\text{Cl}} = \frac{[\text{NO}_3]}{[\text{NO}_3]_{\text{aq}}} / \frac{[\text{Cl}]}{[\text{Cl}]_{\text{aq}}} \right)$ ratio of 1.2×10^{-7} at equilibrium. Clearly, the partitioning of the two ion species over the water-IL system is thermodynamically in favour of NO_3 . This prediction was compared with Co uptake measurements in solutions of different composition. Experiments were performed with feed solutions containing 0.17 M CoCl_2 + 0.2 M NaCl and NaNO_3 ranging from 0.05-0.6 M. The Co uptake as well as the measured feed and raffinate concentrations of NO_3 and Cl are listed in Table 4.2. At low NO_3 levels, virtually all NO_3 is taken up with Cl uptake accounting for the remainder to keep electroneutrality. At higher NO_3 levels, NO_3 remains the dominant anion species that

accompanies Co entering the IL. Note that the uptake of 0.17 M Co requires the uptake of 0.34 M NO₃ or 0.34 M Cl. However, the measured equilibrium ratio values ($P_{\text{NO}_3}^{\text{Cl}} = \frac{[\text{NO}_3]}{[\text{NO}_3]_{\text{aq}}} / \frac{[\text{Cl}]}{[\text{Cl}]_{\text{aq}}}$) in the range of 51±10% are extremely low compared to the theoretical value predicted by the Boltzmann distribution. The difference between the predicted and the measured ratio may be partly due to the fact that the Boltzmann distribution calculation is based on the total dehydration of the two anion species and that entering the IL requires partial dehydration only. More likely, the uptake ratio is dictated by differences in the propensity of complexation with the IL, thereby skewing the distribution ratio in favour of Cl despite its higher dehydration energy. Adding different concentrations of NaCl ranging from 0.05 M to 0.6 M to a feed solution contacting 0.17 M CoCl₂ + 0.2 M NaNO₃ showed the same behaviour, where again all NO₃ is taken up with Cl uptake accounting for the remaining part (see Table 4.D.1 in Appendix).

Table 4.2: Co uptake and equilibrium anion concentrations in the feed and the raffinate after Co extraction from a binary solution containing both NO₃ and Cl. The right-hand column shows the experimental ratio of the anions in the IL and the water phase at equilibrium. The feed solution contained 0.17 M CoCl₂ + 0.2 M NaCl and different concentrations of NaNO₃, ranging from 0.05-0.6 M.

Co uptake [mM]	Anion in feed [mM]		Anion in raffinate [mM]		$(P_{\text{NO}_3}^{\text{Cl}})_{\text{exp}}$
	NO ₃	Cl	NO ₃	Cl	
147	43	511	1	243	53.2
164	89	508	2	277	56.4
159	381	494	68	449	45.8
157	582	491	221	475	50.1

Apart from the differential effect of Cl and NO₃ on Co uptake, the extraction of Co in the presence of NO₃ (and Na, on mass basis is the same concentration as Co) can be described with the same reaction mechanism (Model C. 1:2, Eq. (4.21)) as in the case of Cl. This is shown in Figure 4.12. The MSE value of 5.6 x10⁻⁴ (comparable to the value obtained in Cl-based media) suggests that Model C is applicable for extraction using [P₈₈₈] [Oleate] regardless the nature of the counter anion. The obtained values of K_{eq} and m for Co extraction from the nitrate medium are 3.3 x10⁺² and 0.9 respectively. It is worth noting that the fitted value of the partitioning coefficient m=0.9 is identical to the one obtained with the chloride system. This indicates that the applied modelling approach is consistent. The higher value of K_{eq} obtained by fitting the data of Co uptake from nitrate medium compared to that of chloride medium might indicate that the interaction of IL with Co(NO₃)₂ is stronger than that with CoCl₂. The stronger interaction between Co(NO₃)₂ and IL is mainly shown in the first part of the extraction isotherm, reflecting that the effect of anion is mainly due to the complexation reaction rather than the physical distribution, see Figure 4.11. The implication of this finding in terms of developing a process and

operational conditions, it might be more efficient to perform the LLX process in a nitrate-containing medium.

Figure 4.12: Extraction isotherm of Co obtained in NO_3 medium with the experimental data points fitted by Eq. (4.21) and with a $\text{Co}(\text{NO}_3)_2$:IL ratio of 1:2. Feed solution containing equal concentration of Co and Na on mass basis.

4.3.4 SODIUM EXTRACTION

Figure 4.13 shows the extraction isotherms of Na from chloride and nitrate aqueous media. The results displayed in the figure demonstrate that the extraction of Na from a nitrate aqueous solution is much higher compared to Na extraction from a chloride solution. In this case, the higher Na uptake from a nitrate medium is most probably due to the difference in dehydration enthalpy between the two anion species as Na has no propensity to complex with the IL. FTIR spectrum of the regenerated IL, containing NaCl due to ion exchange between Co and Na during IL regeneration, supports this conclusion, where the spectra of both pure and regenerated IL are overlapping despite the presence of NaCl in the regenerated IL (see Figure 4.A.1). Additionally, the shape of the extraction isotherm of Na which is quite different from that of Co as shown in Figure 4.11 and 4.13. The extraction isotherms of Na from both chloride and nitrate aqueous media are essentially linear. In contrast, the distribution of Co follows a Freundlich-type of isotherm. The difference between the shape of the extraction isotherms of Co and Na indicates a saturation effect due to the complexation of Co with the IL. This also explains that adding CoCl_2 to the NaCl solution inhibits the uptake of Na because Co has a higher propensity for complexation with the IL. This is beside the higher tendency of di-valent cations (e.g., Co) to ion pair, despite their higher hydration energy, compared to mono-valent cations (e.g., Na) [13]. In this study, ion pair formation between Co and Cl anions reduces the hydration energy and stability of Co in the aqueous phase, rendering Co extracted preferentially over Na.

Figure 4.13: Extraction isotherm of Na with IL $[P_{888}][Oleate]$ obtained from solutions containing either the chloride or nitrate-based Na salt. Dashed lines are added to guide the eye of the reader.

4.3.5 EFFECT OF THE PRESENCE OF (MONOVALENT) CATIONS

Apart from the effect of the anion, as discussed in the previous section, the presence of other cations may also affect Co extraction. As before, we will suffice by discussing effects observed during the first cycle with a Co uptake mechanism based on the co-extraction of the monovalent anion in a fixed 1:2 stoichiometry. While the effect of the anion can be direct, since it is co-extracted, the effect of the presence of a cation other than Co is by definition predominantly indirect because it is (almost) not co-extracted [14]. Figure 4.14 shows Co extraction isotherms in chloride (panel A) and nitrate (panel B) media either in the absence or presence of NaCl/NaNO₃ with a Na concentration equal to that of Co in g/L. In both media, the promoting effect of adding the monovalent salting out agent (i.e., NaCl or NaNO₃) is evident. At the highest (equilibrium) feed concentration of 0.16 M, the presence of NaCl or NaNO₃ almost doubles the (equilibrium) Co concentration in the IL. Replacing NaCl by KCl or NH₄Cl, on the other hand, reduces this stimulating effect, reflected in substantially lower distribution coefficients (D), calculated from the equilibrium (total) Co concentrations in the IL and remaining Co in the water phase. For example, adding around 0.05 M of NaCl to a feed solution containing 0.02 M CoCl₂ increases the distribution coefficient from 71 to 449 (Table 4.3). Replacing NaCl by KCl or NH₄Cl reduces this effect, and lowers the distribution coefficient from 499 to 233 and 167, for KCl and NH₄Cl respectively (Table 4.3). In contrast to the anion effect discussed in the previous paragraph, the differential effect of the presence of the monovalent cations Na, K and NH₄ may be interpreted in terms of (de)hydration energy. Adding a salting out agent leaves, after being hydrated, less water molecules available for the hydration of the salt already present and with that facilitates the formation of the extracted species [13, 31]. In the present study, adding NaCl to the CoCl₂ feed solution may reduce the hydration level of Co and with that facilitates the formation of CoCl⁺ and/or CoCl₂, overall resulting

in a higher Co extraction because these salts require less dehydration, as shown in Figure 4.14 panel A. This effect is less pronounced when NaCl is replaced by KCl or NH₄Cl, note Cl concentration is the same in all three cases. In general, the smaller the radius of the ion, the higher (more negative) the hydration energy, an effect due to the increased charge density. With ionic radii of 102, 138 and 161 pm for Na, K and NH₄, respectively, Na has the highest hydration energy. This can explain why the promoting effect of KCl and NH₄Cl are slightly less than that of NaCl as shown in Table 4.3. This means that, the presence of a salting out cation increase the solubility of Co in the organic phase according to the following order: Na > K > NH₄. This series is in line with the reversed Hofmeister series discussed in Appendix 4.E [14]. Similar observations have been reported in the literature where the IL methyltriocylammonium chloride has been used to extract Co, Zn, and Cu from aqueous solutions containing different alkali chloride salts [11, 13].

Figure 4.14: Extraction isotherm of Co with IL [P₈₈₈][Oleate] from chloride (Panel A) or nitrate (Panel B) medium. These data obtained experimentally with and without the addition of NaCl/NaNO₃ as salting-out agent at room temperature.

Table 4.3: The effect of charge density, hydration energies and ionic radius of the salting-out cation on the distribution ratios of Co obtained using [P₈₈₈][Oleate] from feed solution containing 0.02 M CoCl₂ and 0.05 M of NaCl, KCl or NH₄Cl [30, 32].

Cation	ΔH° [kJ/mol]	Ionic radius [pm]	D
No salting-out agent	-	-	71
NH ₄	-307	161	167
K	-322	138	233
Na	-409	102	449

This analysis can also be useful for selecting the right (more efficient) regeneration solution. Especially because the extraction mechanism switches from ion pair in the first cycle to ion exchange with the cation extracted during IL regeneration in the following

cycles as discussed in section 4.3.2 and Chapter 2 [18]. Therefore, considering process development, LLX process would result in a higher Co uptake using sodium salts rather than ammonium or potassium salts as regeneration solution.

4.4 CONCLUSIONS

Reaction model analysis shows that Co is (most) probably extracted, first, as a neutral salt which then interacts with the IL. The extraction of Co has a positive enthalpy and entropy value, which indicates an endothermic spontaneous entropy driven complexation LLX process. The reduction in the free Co activity value with increasing temperature, most likely due to the reduction in the free Co concentration, as well as the reduction in the electrical conductivity with increasing Co concentration in the IL phase support the hypothesized endothermic complexation reaction. Additionally, the extraction behaviour of the IL is affected by (1) the ability of the extracted metal salt to complex with the IL, (2) the nature of the accompanying anion and (3) the presence of a salting-out agent.

APPENDIX 4.A

CHEMICAL ANALYSIS

Figure 4.A.1: FTIR spectra for pure and loaded ionic liquid.

Figure 4.A.2: The visible absorption spectra of CoCl_2 in the aqueous and IL phase.

APPENDIX 4.B

LLX PROCESS BASED ON ACTIVITY DESCRIPTION

The activity coefficient, γ_i , described first by Lewis in 1901 as “the tendency to escape the phase in which it is in”, is an important thermodynamic property which accounts for deviations from ideal behaviour in a mixture of non-ideal substance [33, 34]. It is widely used in evaluating the intermolecular interaction between the solute and solvent [35]. The value of γ_i will be lower than unity ($\gamma_i < 1$) when the intermolecular interaction between the solute and solvent is stronger than those between the solvent molecules, representing a lower tendency of the solute to escape the phase in which it is in. Conversely, the value of γ_i will be higher than unity ($\gamma_i > 1$) when attractive interaction between the solvent molecules are stronger and accordingly a higher tendency of the solute to escape the phase in which it is in. In the ideal solution, the value of γ_i equals unity ($\gamma_i = 1$), when there is either no molecular interaction or where they are all identical.

The coefficient γ_i relates the ionic activity a_i to a concentration c_i according to Eq. (4.B.1) [36]. The activity of a species in a mixture is a measure of its effective concentration in the mixture [33, 34]. When any two phases are brought together, the substance will pass from the phase with the high activity to the phase with the low activity until the activities in both phases are equal (equilibrium state) [34].

$$a_i = c_i \gamma_i \quad (4.B.1)$$

The activity of ions varies with the total ionic strength of the solution. Ionic strength is defined as [36]:

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (4.B.2)$$

In this study, for moderate concentrations, corresponding to ionic strengths in the range 1×10^{-3} to 1×10^{-1} M, the extended version of Debye-Hückel equation has been used to calculate γ_i in the raffinate [36, 37]:

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + B\alpha_i \sqrt{I}} \quad (4.B.3)$$

Where, for ionic strengths above 1×10^{-1} M, the Truesdell-Jones extended Debye-Huckel equation was used to calculate γ_i in the raffinate [36, 37]:

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + B\alpha_i \sqrt{I}} + b_i I \quad (4.B.4)$$

For Co, the values of the empirical parameters α_i and b_i are 6.17×10^{-8} cm and 0.22 respectively, b_i is dimensionless. The constants A and B, the so-called Debye-Hückel parameters involve absolute temperature T and the relative permittivity of the solvent ϵ_r as well as several universal constants [36].

$$A = \frac{1.8248 \times 10^6}{(\epsilon_r T)^{3/2}} \quad (4.B.5)$$

$$B = \frac{50.29 \times 10^8}{(\epsilon_r T)^{1/2}} \quad (4.B.6)$$

Table 4.B.1: The literature values of relative permittivity of water ϵ_r obtained at different temperature and the corresponding calculated Debye-Hückel parameters A and B [38].

T [K]	ϵ_r	A [$M^{-1/2}$]	B [$M^{-1/2} \text{ cm}^{-1}$]
295	79.95	0.50	3.27×10^{-7}
323	70.69	0.53	3.33×10^{-7}
353	60.76	0.58	3.43×10^{-7}

First the activity of the Co in the aqueous phase (assuming all Co is present as Co^{2+}) is calculated at three different temperatures as shown in Figure 4.B.1. This Figure shows that the activity of Co in the aqueous phase hardly changes with temperature. Then, given the measured Co uptake, the activity coefficient of Co in the IL is calculated based on the equilibrium condition in which the Co activity in the raffinate equals the Co activity in the IL. The calculation assumes that in both phases all Co is present in its free form and that the change in temperature hardly affects the activity of Co in the IL as in the aqueous phase (see Figure 4.B.1). The values of the activity coefficients of Co are listed in Table 4.B.2. These coefficients are below unity in both the raffinate and the IL, indicating a strong interaction between the Co ions with both phases. The value of the activity coefficient of Co in the IL is lower than that of Co in the raffinate, indicating that the interaction between Co and the IL is stronger than that between Co and other ion species present in the raffinate. Additionally, the higher the temperature of the LLX process, the lower the ratio of activity coefficients $\gamma_{\text{CoIL}}/\gamma_{\text{Coaq}}$, reflecting a stronger interaction between Co and the IL at higher temperature as shown in Figure 4.B.2.

Figure 4.B.1: The effect of temperature on the calculated Co activity in the aqueous phase (equals to the free Co activity in the IL) at different Co concentration in the raffinate.

Furthermore, similar Co uptake provides different activities at different temperatures (i.e., 295, 323 and 353 K) as shown in Table 4.B.2. The higher the temperature, the lower the activity of Co in the IL phase which could reflect a complexation between Co and the IL. The degree of complexation increases with increasing the temperature, reflecting the endothermic nature of the complexation reaction.

Figure 4.B.2: The effect of temperature on Co activity coefficient ratio $\gamma_{Co_{IL}}/\gamma_{Co_{aq}}$ for different Co concentration in the IL.

Table B.4.2: Molar concentration of Co, Na and Cl, ionic strength in the raffinate and activity (coefficient) in the raffinate and IL. Calculations are based on the equilibrium condition that the activity of Co is the same in both phases.

$[\text{Co}]_{\text{raff}}$ [M]	$[\text{Na}]_{\text{raff}}$ [M]	$[\text{Cl}]_{\text{raff}}$ [M]	I_{raff} [M]	$\gamma_{\text{Co,raff}}$	a_{Co} [M]	$[\text{Co}]_{\text{IL}}$ [M]	$\gamma_{\text{Co,IL}}$	$\gamma_{\text{Co,IL}}/\gamma_{\text{Co,aq}}$
T=295 K								
4.4×10^{-6}	2.2×10^{-2}	2.2×10^{-2}	2.2×10^{-2}	6.0×10^{-1}	2.6×10^{-6}	9.0×10^{-3}	2.9×10^{-4}	4.9×10^{-4}
4.2×10^{-5}	4.4×10^{-2}	4.4×10^{-2}	4.4×10^{-2}	5.2×10^{-1}	2.2×10^{-5}	1.8×10^{-2}	1.2×10^{-3}	2.3×10^{-3}
2.3×10^{-4}	8.0×10^{-2}	8.1×10^{-2}	8.1×10^{-2}	4.5×10^{-1}	1.0×10^{-4}	4.0×10^{-2}	2.6×10^{-3}	5.8×10^{-3}
5.0×10^{-3}	2.0×10^{-2}	3.0×10^{-2}	3.5×10^{-2}	5.3×10^{-1}	2.7×10^{-3}	7.5×10^{-2}	3.5×10^{-2}	6.7×10^{-2}
1.1×10^{-2}	4.0×10^{-2}	6.2×10^{-2}	7.3×10^{-2}	4.4×10^{-1}	4.9×10^{-3}	1.2×10^{-1}	4.0×10^{-2}	9.0×10^{-2}
2.4×10^{-2}	7.8×10^{-2}	1.3×10^{-1}	1.5×10^{-1}	3.9×10^{-1}	9.5×10^{-3}	1.8×10^{-1}	5.1×10^{-2}	1.3×10^{-1}
5.1×10^{-2}	1.6×10^{-1}	2.6×10^{-1}	3.1×10^{-1}	3.5×10^{-1}	1.8×10^{-2}	2.8×10^{-1}	6.4×10^{-2}	1.8×10^{-1}
1.1×10^{-1}	3.2×10^{-1}	5.4×10^{-1}	6.5×10^{-1}	3.4×10^{-1}	3.7×10^{-2}	4.1×10^{-1}	9.0×10^{-2}	2.7×10^{-1}
1.6×10^{-1}	4.0×10^{-1}	7.1×10^{-1}	8.7×10^{-1}	3.5×10^{-1}	5.4×10^{-2}	5.0×10^{-1}	1.1×10^{-1}	3.1×10^{-1}
2.3×10^{-1}	6.0×10^{-1}	1.1×10^0	1.3×10^0	3.9×10^{-1}	9.1×10^{-2}	5.9×10^{-1}	1.6×10^{-1}	4.0×10^{-1}
3.1×10^{-1}	8.1×10^{-1}	1.4×10^0	1.7×10^0	4.6×10^{-1}	1.4×10^{-1}	6.7×10^{-1}	2.1×10^{-1}	4.7×10^{-1}
T=323 K								
2.8×10^{-6}	3.6×10^{-3}	3.6×10^{-3}	3.6×10^{-3}	7.7×10^{-1}	2.1×10^{-6}	2.0×10^{-3}	1.1×10^{-3}	1.4×10^{-3}
1.7×10^{-5}	1.4×10^{-2}	1.4×10^{-2}	1.4×10^{-2}	6.3×10^{-1}	1.1×10^{-5}	8.0×10^{-3}	1.3×10^{-3}	2.2×10^{-3}
4.4×10^{-5}	3.0×10^{-2}	3.1×10^{-2}	3.1×10^{-2}	5.3×10^{-1}	2.3×10^{-5}	1.7×10^{-2}	1.4×10^{-3}	2.6×10^{-3}
7.8×10^{-4}	1.5×10^{-1}	1.5×10^{-1}	1.5×10^{-1}	3.7×10^{-1}	2.9×10^{-4}	8.4×10^{-2}	3.5×10^{-3}	9.3×10^{-3}
4.0×10^{-3}	3.0×10^{-1}	3.1×10^{-1}	3.1×10^{-1}	3.3×10^{-1}	1.3×10^{-3}	1.7×10^{-1}	8.0×10^{-3}	2.4×10^{-2}
1.5×10^{-2}	4.6×10^{-1}	4.9×10^{-1}	5.0×10^{-1}	3.2×10^{-1}	4.9×10^{-3}	2.4×10^{-1}	2.0×10^{-2}	6.4×10^{-2}
3.4×10^{-2}	6.1×10^{-1}	6.8×10^{-1}	7.1×10^{-1}	3.2×10^{-1}	1.1×10^{-2}	3.1×10^{-1}	3.5×10^{-2}	1.1×10^{-1}
1.1×10^{-1}	1.1×10^0	1.3×10^0	1.4×10^0	3.8×10^{-1}	4.1×10^{-2}	4.8×10^{-1}	8.4×10^{-2}	2.2×10^{-1}
2.1×10^{-1}	1.5×10^0	1.9×10^0	2.1×10^0	5.0×10^{-1}	1.0×10^{-1}	6.4×10^{-1}	1.6×10^{-1}	3.3×10^{-1}
T=353 K								
1.8×10^{-6}	3.6×10^{-3}	3.6×10^{-3}	3.6×10^{-3}	7.5×10^{-1}	1.3×10^{-6}	2.0×10^{-3}	6.7×10^{-4}	8.9×10^{-4}
1.5×10^{-5}	1.4×10^{-2}	1.4×10^{-2}	1.4×10^{-2}	6.0×10^{-1}	9.4×10^{-6}	8.0×10^{-3}	1.2×10^{-3}	1.9×10^{-3}
4.0×10^{-5}	3.0×10^{-2}	3.1×10^{-2}	3.1×10^{-2}	5.1×10^{-1}	2.0×10^{-5}	1.7×10^{-2}	1.2×10^{-3}	2.4×10^{-3}
6.3×10^{-4}	1.5×10^{-1}	1.5×10^{-1}	1.5×10^{-1}	3.4×10^{-1}	2.2×10^{-4}	8.4×10^{-2}	2.6×10^{-3}	7.5×10^{-3}
2.2×10^{-3}	3.0×10^{-1}	3.1×10^{-1}	3.1×10^{-1}	3.0×10^{-1}	6.6×10^{-4}	1.7×10^{-1}	4.0×10^{-3}	1.3×10^{-2}
8.3×10^{-3}	4.6×10^{-1}	4.7×10^{-1}	4.8×10^{-1}	2.8×10^{-1}	2.4×10^{-3}	2.5×10^{-1}	9.6×10^{-3}	3.4×10^{-2}
1.9×10^{-2}	6.1×10^{-1}	6.5×10^{-1}	6.6×10^{-1}	2.8×10^{-1}	5.3×10^{-3}	3.2×10^{-1}	1.7×10^{-2}	5.9×10^{-2}
6.2×10^{-2}	1.1×10^0	1.2×10^0	1.2×10^0	3.2×10^{-1}	2.0×10^{-2}	5.3×10^{-1}	3.7×10^{-2}	1.2×10^{-1}
1.6×10^{-1}	1.5×10^0	1.8×10^0	2.0×10^0	4.1×10^{-1}	6.5×10^{-2}	6.9×10^{-1}	9.5×10^{-2}	2.3×10^{-1}

APPENDIX 4.C

1. LLX PROCESS BASED ON CONDUCTIVITY DESCRIPTION

Conductivity measurements can also be a useful tool to investigate metal complexation in ILs. This technique is widely applied due to its precision, simplicity, and low cost [39]. The conductivity of a solution is a function of the number of ions present, as well as their mobility and valence [40]. The electrical conductivity of the IL as a function of totally dissolved CoCl_2 in the range of 0.02 to 0.27 M is shown Table 4.C.1. The measured electrical conductivities are compared with calculated theoretical values, assuming that all Co and Cl in the IL are present as free ions, obtained using the Nernst-Einstein equation and assuming ideal solution behaviour. Additionally, the Stokes-Einstein equation is used to calculate the IL self-diffusivity and the Wilke Chang equation to calculate the Co and Cl diffusivity in the IL phase (see section 2 in Appendix 4.C) [41-43]. Calculated (self) diffusivities D_i are used for the calculation of the conductivity.

$$\kappa = \sum_i \Lambda_{m,i}^0 c_i \varphi = \left(\frac{F^2 \varphi}{RT} \right) \sum_i D_i z_i^2 c_i \quad (4.C.1)$$

Table 4.C.1: Physical properties of fresh and loaded IL with different Co concentrations.

Physical properties	Fresh IL	Co concentration in IL [M]		
		0.02	0.17	0.27
μ [Pa·sec]	0.13	0.14	0.23	0.34
κ measured [mS/cm]	0.19	0.16	0.13	0.07
κ calculated [mS/cm]	0.25	0.51	1.75	2.01
Co diffusivity [m/sec ²]	-	6.48×10^{-11}	4.05×10^{-11}	2.75×10^{-11}
Cl diffusivity [m/sec ²]	-	6.85×10^{-11}	4.21×10^{-11}	2.87×10^{-11}

Note that fresh IL already demonstrates a relatively high conductivity, expressing the electrolytic nature of the IL. Since the cations and anions of the ILs may reside in two states either free (ionized) or bound (neutral complex) with an interstate exchange [44]. Surprisingly, adding CoCl_2 to the IL decreased the measured conductivity substantially. At a constant temperature of 295 K, the measured conductivity of fresh IL decreased from $0.19 \text{ mS}\cdot\text{cm}^{-1}$ to 0.16, 0.13 and $0.07 \text{ mS}\cdot\text{cm}^{-1}$ after loading the IL with 0.02, 0.17 and 0.27 M Co, respectively. This observation may be explained by hypothesizing (1) that CoCl_2 is extracted as a neutral salt and remains associated and (2) that a neutral complex is formed between the IL and CoCl_2 , apparently resulting in a reduction of the conductivity of the IL. Complexation seems also in accordance with the observed viscosity increase at higher CoCl_2 concentration (Figure 4.C.1). In contrast to the measured lower conductivity at higher CoCl_2 , the calculated electrical conductivity showed the opposite behaviour, even with the viscosity change taken into account. This observation supports the occurrence of

a complexation reaction causing a drastic reduction in total number of free charge carriers present, as in line with the hypothesized extraction mechanisms discussed in section 4.3.1.

2. CALCULATING DIFFUSION COEFFICIENTS

The Stokes-Einstein equation is used to calculate the IL self-diffusivity. This equation correlates the self-diffusion coefficient of a component to the effective hydrodynamic radius r , zero shear rate viscosity μ_s and temperature T [41-43]:

$$D_c = \frac{k_B T}{6\pi r_c \xi_c \mu_s} \quad \text{or} \quad D_a = \frac{k_B T}{6\pi r_a \xi_a \mu_s} \quad (4.C.2)$$

Where, k_B is the Boltzmann constant. r_c , r_a , ξ_c and ξ_a are the cationic and anionic radius and micro-viscosity factors, respectively. The micro-viscosity factors ξ_c and ξ_a are related to the specific interactions between the mobile ions in the ILs, which are governed by interionic hydrogen-bonding and Coulombic interactions [41]. The value of ξ_c and ξ_a used in Eq. (4.C.2) is 2/3 [43]. The cationic and anionic radii are estimated as follows assuming anion and cation have the same density as that of the solvent (IL) [43]:

$$r_c = \frac{1}{2} \left(\frac{M_c}{\rho_s N_A} \right)^{1/3} \quad \text{or} \quad r_a = \frac{1}{2} \left(\frac{M_a}{\rho_s N_A} \right)^{1/3} \quad (4.C.3)$$

Where, M is the molecular weight of the cation/anion of the IL, ρ_s is the density and N_A is Avogadro number.

The Wilke Chang equation is used to calculate the Co and Cl diffusivity in the IL phase:

$$D_i = \frac{7.4 \times 10^{-8} (\Phi_s M_s)^{1/2} T}{\mu_s V_i^{0.6}} \quad (4.C.4)$$

Where, M_s is the the molecular weight of the solvent (IL), V_i is the molar volume of solute at normal boiling point and Φ_s is the association parameter for the solvent. Φ_s is estimated as follows:

$$\Phi_s = \sum_i y_i M_i \Phi_i \quad (4.C.5)$$

Where, y_i , M_i and Φ_i are the mole fraction, molecular weight and association parameter of IL and water (10 wt.%) in the organic phase. Table 4.C.2 lists the parameters used to calculate the IL self-diffusivity and to calculate the Co and Cl diffusivity in the IL phase.

Table 4.C.2: paramters used to calcuale the IL self-diffusivity and the Co and Cl diffusivity in the IL phase [45-47].

Parameters	Value	Unit
M_c	484	[g/mol]
M_a	281	[g/mol]
M_s	765	[g/mol]
M_{water}	18	[g/mol]
ρ_s	0.897	[g/cm ³]
Φ_{IL}	2.26	[-]
Φ_{water}	1	[-]
γ_{IL}	0.17	[mol IL/mol solvent]
γ_{water}	0.83	[mol water/mol solvent]
V_{Co}	6.7	[cm ³ /mol]
V_{Cl}	21.6	[cm ³ /mol]
V_{CoCl_2}	15.5 (used in Chapter 5)	[cm ³ /mol]

Figure 4.C.1: IL viscosity as function of Co concentration.

APPENDIX 4.D

BOLTZMANN DISTRIBUTION CALCULATION

The NO_3 over Cl selectivity of the IL, $P_{\text{NO}_3}^{\text{Cl}}$, is given by:

$$P_{\text{NO}_3}^{\text{Cl}} = \frac{[\overline{\text{NO}_3}]/[\text{NO}_3]_{\text{aq}}}{[\overline{\text{Cl}}]/[\text{Cl}]_{\text{aq}}} \quad (4.D.1)$$

Where; $[\overline{\text{NO}_3}]$, $[\text{NO}_3]_{\text{aq}}$, $[\overline{\text{Cl}}]$ and $[\text{Cl}]_{\text{aq}}$ are the equilibrium concentrations of nitrate and chloride ions in the IL and the aqueous phase, respectively [48]. Table 4.2 and 4.D.1 list the values of the equilibrium concentrations of NO_3 and Cl in the aqueous and the IL phase for feed solutions containing either 0.17 M CoCl_2 + 0.2 M NaCl and different concentrations of NaNO_3 , ranging from 0.05-0.6 M or 0.17 M CoCl_2 + 0.2 M NaNO_3 and different concentrations of NaCl, ranging from 0.05-0.6 M. The experimentally obtained values of $P_{\text{NO}_3}^{\text{Cl}}$ are compared with calculated values based on the assumption that the concentration ratio of both ion species in the IL and water phase follow a Boltzmann distribution, as shown in Eq. (4.D.2) [49]:

$$P_{\text{NO}_3}^{\text{Cl}} = \frac{[\overline{\text{NO}_3}]/[\text{NO}_3]_{\text{aq}}}{[\overline{\text{Cl}}]/[\text{Cl}]_{\text{aq}}} = \exp \left[\frac{\Delta_{\text{hyd}}G_{\text{NO}_3} - \Delta_{\text{hyd}}G_{\text{Cl}}}{RT} \right] \quad (4.D.2)$$

Where, $\Delta_{\text{hyd}}G_{\text{NO}_3}$ and $\Delta_{\text{hyd}}G_{\text{Cl}}$ represent the change in Gibbs free energy of (total) dehydration of NO_3 and Cl, equal to 300 kJ/mol and 340 kJ/mol, respectively [50].

Table 4.D.1: Co uptake and anion concentrations in the feed and the raffinate after Co extraction from a binary solution containing both NO_3 and Cl. The right-hand column shows the experimental ratio of the anions in the IL and the water phase at equilibrium. The feed solution contained 0.17 M CoCl_2 + 0.2 M NaNO_3 and different concentrations of NaCl, ranging from 0.05-0.6 M.

Co uptake [mM]	Anion in feed [mM]		Anion in raffinate [mM]		$(P_{\text{NO}_3}^{\text{Cl}})_{\text{exp}}$
	NO_3	Cl	NO_3	Cl	
158	181	350	6	226	51.6
158	184	401	5	260	61.0
170	187	702	9	530	60.1
160	181	874	12	714	63.9

APPENDIX 4.E

INTERPRETING ANION AND CATION EFFECT BY HOFMEISTER SERIES

For the Co salts studied in section 4.3.3 and 4.3.5, the identity of the anion and salting out cation strongly influences the extraction of Co. As indicated by the results reported in section 4.3.3, the observed difference in Co uptake can be explained by the propensity of the metal salt to interact with the IL. Additionally, the results are also in line with the Hofmeister series. Hofmeister describes the effect of salt anions and cations on the stability and solubility of proteins or other types of molecules in an aqueous solution [16]. Figure 4.E.1 shows the ranking order of effectiveness of the anion and the salting out cation according to the Hofmeister series.

Figure 4.E.1: The effect of the salt anion and cation on protein solubility in an aqueous solution according to the Hofmeister series. Note: red coloured ions are investigated in the present study [51].

In this study considering the extraction of Co to the IL phase, it is concluded that the ranking order of effectiveness of the anion and the salting out cation corresponds to the Hofmeister series but with a reversed order (reversed Hofmeister) [16]. In other words, the ranking order of effectiveness of ions present in the aqueous phase on the solubility of Co in the organic phase follows the reversed Hofmeister series. For instance, the presence of NO_3^- in the aqueous solution reduces the stability and solubility of Co in the aqueous phase more than Cl does, resulting in a higher Co uptake to the IL from NO_3^- than Cl media. Similarly, the presence of a salting out cation reduces the solubility of Co in the aqueous phase according to the following order: $\text{Na} > \text{K} > \text{NH}_4^+$. This is in line with the conclusions drawn in section 4.3.5, where the distribution coefficient of Co is higher in the presence of Na. It is worth noting that the effect of the salting out cation is indirect and induced by an excluded volume mechanism in which the water will preferentially solvate the cation (e.g., Na) leaving less water for the Co and squeezes the Co out of the aqueous phase [14]. Contrary, the effect of the anion can be direct (first cycle) or indirect (from second cycle on) depending on its ability to interact with the molecule (Co) via ion pairing in the aqueous phase. In the latter case, the reverse Hofmeister effect is dominated by Coulombic interactions where the less solvated anions seem to pair most strongly with Co [14]. Ion pairings will reduce the net charge of the Co salt and accordingly will lower its solubility and push it out of the aqueous phase.

Nomenclature

Symbols	Description	Unit
a_i	Activity of ion i	M
C_i	Molar concentration of charged body	M or mol/m ³
D	Distribution coefficient	-
D_i	Diffusion coefficient	m ² /sec or cm ² /s
F	Faraday constant = 9.6485×10^4	coulomb/mol
ΔG°	Free Gibbs energy	J/mol
ΔH°	Enthalpy	J/mol
I	Ionic strength or ion in aqueous solution	M
K_{cc}	Average correlation value of the cross-correlation matrix	-
K_{eq}	Equilibrium constant	-
m	Partition coefficient	-
MSE	Mean square error	-
R	Gas constant 8.31446	J/mol K
ΔS°	Entropy	J/mol
T	Temperature	K
wt.	weight fraction	%
Z_i	Charge number or valance of ion i	-
Greek letters		
κ	Electrical conductivity	S/m
γ_i	Activity coefficient	-
ρ	Density	kg/m ³
ϵ_r	Relative permittivity	-
$\Lambda_{m,i}^0$	Molar limiting conductivity of ion i	S/m
μ	Viscosity	Pa.sec
φ	Degree of dissociation $0 < \varphi < 1$	-
Subscripts		
aq	Aqueous phase	
exp	Experimental	
int	Interface	
raff	Raffinate	

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CHAPTER 5

KINETIC ANALYSIS OF AN IONIC LIQUID-BASED METAL EXTRACTION PROCESS

All models are wrong but some are useful

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ABSTRACT

In this chapter a LLX process has been investigated based on experimental analysis and kinetic modelling. The purpose of this investigation is (1) to understand the mass transfer behaviour, (2) to determine the rate limiting step via evaluating different mass transfer models, and (3) estimate the mass transfer and kinetic parameters. This has been discussed in the context of the extraction of Co by the IL $[P_{888}][Oleate]$ as an example of LLX with chemical reaction. Mass transfer models, with and without a chemical reaction, are evaluated based on a statistical cross-validation method in which the outcome involves the effect of the following parameters: column lengths, droplet diameter, droplet rising velocity and continuous and dispersed phase concentrations on Co uptake. This method reveals that a single parameter model based on external mass transfer can describe the forward extraction of Co for the whole data set sufficiently accurate (error $\pm 30\%$) regardless of the studied operational conditions.

5.1 INTRODUCTION

Extraction columns are widely used in chemical, hydrometallurgical, petrochemical, and pharmaceutical separation processes due to their low energy consumption, high efficiency and simplicity of operation [1-3]. However, lack of knowledge regarding hydrodynamics, mass transfer, chemical kinetics and the underlying thermodynamics limits the optimization of these columns. This is because studying the extraction process on large scale is expensive and time-consuming since it requires rather large quantities of chemicals and a large number of pilot experiments. Using a single droplet extraction column is a promising method to understand mass transfer behaviour in LLX system [4].

Metal extraction, representing a conventional industrial process, can be considered a general framework for studying mass transfer occurring with reaction in columns. This type of investigations is usually performed using $\text{ZnSO}_4/\text{D}_2\text{EHPA}/\text{Kerosene}$, which is recommended by the European Federation of Chemical Engineering as a standard test system [2, 5]. The present study focuses on the extraction of Co due to its significant value in supporting economic growth and development and reducing environmental impact arising from metallurgical, and mining industries [6, 7]. In this chapter, $[\text{P}_{888}][\text{Oleate}]$ is used which demonstrates a high and selective extraction efficiency towards Co over several consecutive batch cycles [7, 8].

The rate of LLX with chemical reaction is a complex function of mass transfer rate and chemical reaction kinetics. Mass transfer and chemical reaction occur at or across the interface of each droplet where fluid dynamics and mass transfer are inseparably associated with interfacial properties and phenomena, such as droplet deformation, internal circulation, oscillation or Marangoni instabilities, among others [9]. Mass transfer can be described by the two film theory, penetration theory or surface renewal theory [10]. Reactive extraction is defined by a chemical reaction which occurs either at the interface “Heterogeneous reaction” or within the bulk phase “Homogeneous reaction”. For a heterogenous system, two extreme conditions exist regarding the rate controlling mechanisms of the extraction: 1) the diffusional regime where the mass transfer controls the extraction rate and 2) the chemical regime in which the kinetics of the chemical reaction is controlling. A reaction in the bulk results in a higher capacity as the extracted solute is “stored” by the chemical reaction and it can maintain the high initial flux for a longer period of time as it reduces the concentration of “free” solute.

In a single droplet extraction column, the estimation of the mass transfer coefficients depends mainly on the knowledge of mass transfer behaviour [1]. Even though, a large number of studies can be found in literature with respect to theoretical models and empirical correlations for predicting the mass transfer coefficients, the predictions

show both success and failure when compared with the experimental results [1, 11, 12]. Moreover, it is usually claimed that it is difficult to assess the predictive ability of literature correlations, since the range of their applications is not always known [11]. This introduces extra difficulty in selecting the right model. Kumar and Hartland have published a collection of mass transfer correlations for a rising droplet [11]. Mass transfer correlations for the continuous phase are expressed in the form of $Sh_c = f(Re, Sc_c, \kappa)$ where κ is the viscosity ratio between the dispersed and continuous phase. The Newman model applies to rigid spherical droplets without internal circulation [13]. The mass transfer intensifying effect of droplet internal circulation is taken into account by (1) Kronig-Brink who proposed a model for laminar diffusion with internal circulation and (2) Handlos-Baron who proposed a model in which turbulence-like disturbance is added to the internal circulation [9, 14, 15]. To overcome the limited prediction of the Newman model, Zheng et al., implemented an enhancement factor reflecting the effect of initial solute concentration, drop rise velocity and interfacial instability [16, 17]. Wegener et al., improved the Handlos-Baron model by introducing a concentration dependent parameter accounting for the influence of the initial solute concentration difference between the aqueous and organic phase and to characterize the intensity of the Marangoni effect [18]. Anari et al., developed a correlation for an effective diffusion coefficient to reveal the effect of chemical reaction on mass transfer rate [2].

In this chapter we investigated the mass transfer and reaction kinetic of Co extraction by $[P_{8888}][Oleate]$ to determine the rate limiting step and to evaluate whether adding a chemical reaction to the mass transfer model is necessary to describe the forward and backward extraction. Furthermore, we have also examined whether the stagnant and internal circulation models and correlations found in the literature provide a satisfactorily prediction of the experimental data. The two-film theory has been applied to predict Co uptake using (1) an internal circulation model and correlation from literature, and (2) a mass transfer model with and without chemical reaction. Both options are evaluated using a statistical cross-validation (CV_s) method as described in the work of Slotboom et al., [19]. CV_s permits the calculation of associated mass transfer and kinetic parameters, and with that it identifies the rate limiting step(s) of the overall process. This is achieved via studying the extraction of Co into single IL droplets rising in a single droplet extraction column with considerations for equilibria, molecular diffusion, convective mass transfer and reaction kinetics. The experimental data set consists of more than 50 experiments under different experimental conditions regarding column lengths, droplet rising velocity (both affecting the contact time), droplet diameter, and continuous and dispersed phase Co concentration. This lumped data set was then fitted by different models using the statistical cross-validation method as selection tool evaluating the predictive capability and variance of each model.

5.2 THEORY

There are different theories concerning mass transfer among phases, such as the two-film theory, the penetration theory, and the surface renewal theory. In this study, the two-film theory was used to model the physical mass transfer of Co from the aqueous phase into the IL droplet phase. This theory was first developed in 1924 by Lewis and Whitman and it hypothesizes the existence of a distinct interface between the two phases, covered by a film with thickness (δ) on both sides of the interface [20]. The theory involves the following assumptions: (1) mass transfer occurs by molecular diffusion across the films; (2) bulk concentration in both phases is homogeneous with respect to solute beyond this film; (3) mass transfer across the film occurs under steady state conditions [21, 22]. Accordingly, for convective mass transfer, the concentration profile is linear as shown in Figure 5.1 (neglecting the curvature effect of the droplet since $\delta < d$). Many transport processes involve the mass transfer of molecular species coupled to the disappearance or appearance of the particular species through a heterogeneous and/or homogeneous chemical reaction.

Figure 5.1: Schematic representation of the two-film theory. Superscript c and d refer to the continuous and dispersed phase, respectively; the subscript int refers to the concentration at the interface.

Using a single droplet extraction column as a prototype, the process of mass transfer has been modelled using a non-stationary mass balance of the free Co transferred as neutral partially hydrated salt $CoCl_2$ into an IL droplet of specific area a . Assuming that the single droplet is a rigid sphere, Co uptake is calculated based on the overall driving force between the bulk concentrations as follows:

$$\frac{dC_{CoCl_2}^d}{dt} = K a (C_{CoCl_2}^{*d} - C_{CoCl_2}^d) \quad (5.1)$$

Where, the overall mass transfer coefficient K is defined as the follows:

$$\frac{1}{K} = \frac{m}{k_c} + \frac{1}{k_d} \quad (5.2)$$

The partitioning coefficient m , which is defined as the ratio of the equilibrium concentrations of the free $CoCl_2$ at the interface (i.e., free $CoCl_2$ salt in the dispersed phase ($C_{CoCl_2}^{*d}$) to free Co in the continuous phase (C_{Co}^{*c}), is expressed as the follows:

$$m = \frac{[\overline{CoCl_2}]}{[Co_{aq}^{2+}]} = \frac{C_{CoCl_2}^{*d}}{C_{Co}^{*c}} \quad (5.3)$$

Afterwards, the metal salt diffuses into the bulk of the organic phase where it exhibits a homogenous interaction with the anionic part (i.e., carboxyl group) of the IL according to the hypothesized mechanism discussed in chapter 4. The overbars represent the organic phase.

The corresponding equilibrium constant K_{eq} for the formation of $([\overline{P_{888}}][\overline{Oleate}])_2 \overline{CoCl_2}$ is defined by Eq. (5.5). The total $CoCl_2$ in the IL phase includes both the free and the part complexed with IL ($[\overline{CoCl_2}]_{Total} = [\overline{CoCl_2}] + [([\overline{P_{888}}][\overline{Oleate}])_2 \overline{CoCl_2}]$). Likewise, the total IL includes both the free and the complexed IL ($[\overline{P_{888}}][\overline{Oleate}]_{Total} = [\overline{P_{888}}][\overline{Oleate}] + 2 [([\overline{P_{888}}][\overline{Oleate}])_2 \overline{CoCl_2}]$).

$$K_{eq} = \frac{([\overline{P_{888}}][\overline{Oleate}])_2 \overline{CoCl_2}}{[\overline{CoCl_2}] [\overline{P_{888}}][\overline{Oleate}]^2} = \frac{C_{CoCl_2-IL}^d}{C_{CoCl_2}^{*d} (C_{IL}^d)^2} \quad (5.5)$$

This homogenous reaction occurs in parallel with the mass transfer. In this case, the reaction kinetics are coupled to the mass transfer equation to calculate the free $CoCl_2$:

$$\frac{dC_{CoCl_2}^d}{dt} = K a (C_{CoCl_2}^{*d} - C_{CoCl_2}^d) - r_{CoCl_2-IL} \quad (5.6)$$

The formation of the $\text{CoCl}_2\text{-IL}$ complex ($C_{\text{CoCl}_2\text{-IL}}^d$) is shown in Eq. (5.4), where K_{eq} is calculated according to Eq. (5.5):

$$r_{\text{CoCl}_2\text{-IL}} = \frac{dC_{\text{CoCl}_2\text{-IL}}^d}{dt} = k_r \left(C_{\text{CoCl}_2}^d (C_{\text{IL}}^d)^2 - \frac{C_{\text{CoCl}_2\text{-IL}}^d}{K_{\text{eq}}} \right) \quad (5.7)$$

The consumption of IL:

$$\frac{dC_{\text{IL}}^d}{dt} = -2 r_{\text{CoCl}_2\text{-IL}} \quad (5.8)$$

The total Co uptake in the dispersed phase is calculated as the following:

$$C_{\text{CoCl}_2\text{-Total}}^d = C_{\text{CoCl}_2}^d + C_{\text{CoCl}_2\text{-IL}}^d \quad (5.9)$$

These differential equations are solved using the following initial conditions:

For the free CoCl_2 in the dispersed phase:

$$C_{\text{CoCl}_2}^d = C_{\text{CoCl}_2}^d \big|_{t=0} \quad (5.10)$$

For the Complexed Co with IL in the dispersed phase:

$$C_{\text{CoCl}_2\text{-IL}}^d = C_{\text{CoCl}_2\text{-IL}}^d \big|_{t=0} \quad (5.11)$$

For the IL in the dispersed phase:

$$C_{\text{IL}}^d = C_{\text{IL}}^d \big|_{t=0} \quad (5.12)$$

Where $C_{\text{CoCl}_2}^d \big|_{t=0}$ and $C_{\text{CoCl}_2\text{-IL}}^d \big|_{t=0}$ are the initial concentrations of the free and complexed Co in the dispersed phase, respectively, both zero in the case of using fresh IL. When using preloaded IL, the initial free CoCl_2 and initial $\text{CoCl}_2\text{-IL}$ complex equal their equilibrium concentrations, both defined by the equilibrium constant K_{eq} . $C_{\text{IL}}^d \big|_{t=0}$ is the initial concentration of the free IL which equals 1.06 M in the case of using fresh IL and $(1.06 - 2C_{\text{CoCl}_2\text{-IL}}^d \big|_{t=0})$ in case of using the preloaded IL.

The last case considered in this study is evaluated based on the assumption that all the extracted CoCl_2 salt in the dispersed phase is free and that there is no reaction between the extracted salt and IL. Therefore, the mass model has also been evaluated using the distribution coefficient (D). Since the distribution coefficient in this LLX system is variable, reflecting that Eq. (5.2) is not valid. Hence the Co uptake has been calculated using a mass

transfer model that employs individual mass transfer coefficient for the continuous and the dispersed phase and where the driving force is defined as the concentration gradient between the bulk and the interface of the continuous phase and the concentration gradient between the interface and the bulk of the dispersed phase respectively:

$$\frac{dC_{CoCl_2}^d}{dt} = k_c a (C_{Co}^c - C_{Co,int}^c) \quad (5.13)$$

And,

$$\frac{dC_{CoCl_2}^d}{dt} = k_d a (C_{CoCl_2,int}^d - C_{CoCl_2}^d) \quad (5.14)$$

The solute flux out of the continuous phase must equal the flux of the solute in the dispersed phase. Combining Eqs. (5.13) and (5.14), results in:

$$k_c a (C_{Co}^c - C_{Co,int}^c) = k_d a (C_{CoCl_2,int}^d - C_{CoCl_2}^d) \quad (5.15)$$

Both Co concentrations at the interface are at equilibrium and related by the extraction isotherm. The equilibrium correlation between $C_{Co,int}^c$ and $C_{CoCl_2,int}^d$ in [mol/L] is obtained by fitting the extraction isotherm of Co by a 2nd order polynomial, resulting in:

$$C_{Co,int}^c = 0.7635(C_{CoCl_2,int}^d)^2 - 0.051C_{CoCl_2,int}^d + 0.0029 \quad (5.16)$$

Note, at equilibrium the interface concentration is equal to the bulk concentration.

In this chapter, three possible cases were considered regarding the transfer of Co from the continuous phase to the IL droplet. In the first case, a mass transfer model has been evaluated assuming that all the extracted $CoCl_2$ is present in the dispersed phase as free salt and that there is no reaction between the extracted salt and the IL. In the last two cases a mass transfer model has been evaluated assuming that $CoCl_2$ diffuses into the dispersed phase as a free salt and then reacts with the IL (i.e., $CoCl_2$ is present in the dispersed phase as free salt and as complex with IL). These cases are:

1. Mass transfer model using a variable distribution coefficient D (assuming no reaction between $CoCl_2$ and IL). This model has been evaluated using literature correlations for mass transfer coefficients with internal circulation.
2. Mass transfer model using m (assuming that the homogenous reaction is slow relative to the mass transfer in the time frame of the extraction). This model has been evaluated (i) using literature correlations for mass transfer coefficients with

internal circulation and (ii) using the CV_5 method for estimating the mass transfer coefficients.

3. Mass transfer with homogenous reaction model using m (full model).

5.2.1 PARAMETER ESTIMATION

The five-fold Cross-Validation (CV_5) method was used to determine the goodness of fit statistically [19, 23]. This method involves dividing the total dataset randomly into 5 unique folds (groups) of approximately equal size. One-fold is used for validation (test set) and the remaining four folds are used for fitting the model (training set). This procedure is repeated 5 times, where each time a different group of observations is assigned to be the validation set. The main purposes behind using this method are (1) to determine the goodness of each model in predicting data points outside of its trained dataset and, (2) to determine the deviation of the parameters when fitted on a specific dataset.

For each training set, parameter estimation was performed using the mean square error (MSE) regression method. The MSE is the average squared difference between the estimated parameter values and the actual value (obtained experimentally) as shown in Eq. (5.17). Global Optimization Toolbox of MATLAB® 2017b was used to obtain the global minimum. GlobalSearch is initiated with the fmincon solver and the Sequential Quadratic Programming (SQP) algorithm.

$$MSE_k = \frac{1}{N} \sum_{i=1}^N (C_{exp,i} - C_{model,i})^2 \quad (5.17)$$

CV_5 is calculated by averaging the five MSEs of the test sets as shown in Eq. (5.18):

$$CV_5 = \frac{1}{5} \sum_{k=1}^5 MSE_k \quad (5.18)$$

The best model is the one which can predict experiments outside the training set good rather than fit a specific dataset perfectly. In Five-fold cross-validation, a lower CV_5 value indicates a better predictive ability of the model. The selected parameters per model are the ones with the lowest MSE for the whole dataset and the corresponding MSE is called MSE_{best} . This set of parameters is considered as the absolute best model for the total dataset.

The standard deviation of each model parameter is calculated as the standard deviation over the five fits. The average standard deviation of a model over five fits is defined as the following:

$$\sigma_{p,avg} = \frac{1}{N_p} \sum_{i=1}^{N_p} \frac{\sigma_{p_i}}{|P_i|} \quad (5.19)$$

Where N_p is the number of fitted parameters, σ_{p_i} is the standard deviation of each parameter over the 5 fits and P_i is the fitted parameter of the MSE_{best} fit. The value of $\sigma_{p,avg}$ represents the percentage of deviation of the obtained fitting parameters of the same model when regressed five times over essentially the same dataset. The lower the value of $\sigma_{p,avg}$ the less the parameters are changing when a completely new dataset is taken, on average.

The dependency of a fitting parameter to another can be determined by the average correlation number of the cross-correlation matrix (K_{cc}) which is calculated as follows:

$$K_{cc} = \frac{1}{N_p^2} \sum_{i=1}^{N_p} |CC_i| \quad (5.20)$$

The value of cross-correlation matrix ranging between -1 and 1. The closer the cross-correlation value is to 1 or -1, the higher the dependency of the fitting parameters on each other. The closer the cross-correlation value is to 0, the lower the dependency of the fitting parameters on each other.

5.3 EXPERIMENTAL

5.3.1 MATERIALS AND ANALYSIS

Tetraoctylphosphonium bromide (> 95 %) was purchased from IoLiTec; sodium chloride, ammonium chloride, and nitric acid (69 %) from VWR Chemicals; oleic acid (90 %), perchloric acid (70%) and cobalt (II) chloride hexahydrate (98 %) from Alfa Aesar. MilliQ water ($\geq 18 \text{ M}\Omega\cdot\text{cm}$) was obtained from a Millipore Milli-Q® Biocel, which uses a Qgrade® column. All chemicals were used as received, without any further purification. Tetraoctylphosphonium oleate [P_{888}][Oleate] was synthesized according to the procedure described in Chapter 3 [7].

The aqueous phases after each extraction process were analysed by a Metrohm IC Compact 761 ion chromatograph (detection range: 0.1-80 mg/L) and a Perkin Almer Optima 5300 DV inductive coupled plasma optical emission spectrometry (ICP-OES) (detection range: 0.025 - 10 mg/L). The organic phase was digested using a Milestone Ethos Easy microwave digester and analysed using the same instruments as applied for the aqueous phase.

5.3.2 EXTRACTION

The mass transfer experiments were carried out in laboratory scale glass columns of different heights (50, 300, 670, 1170 and 1500 mm), as illustrated in Figure 5.2. The inner diameter of the column is 18 mm which is large enough to avoid wall effects in the experiments. The column is equipped with a jacket where the temperature of the system was adjusted by an external water bath. The droplets are dosed by an Aladdin Syringe Pump, type AL1000-220. The droplets were formed at the tip of a stainless-steel nozzle with the pump running at the appropriate rate. Different nozzle sizes ranging from G8 to G23 were used to examine the effect of droplet size. G18 was selected as standard nozzle for all other experiments since it provided the smallest stable droplets at 1 ml/min. At the top of the column an inverted glass funnel was installed to collect the IL droplet in a way to minimize the interfacial area between both phases and thus reduce extra mass transfer occurring during coalescence.

In this investigation, the organic phase was chosen as the phase to be dispersed as it has a higher viscosity compared to the aqueous phase and is more expensive. The average droplet volume and diameter were determined by counting the number of droplets formed given certain volumetric flow, while assuming all droplets to be rigid perfect spheres of constant volume. The droplet slip velocity was calculated by measuring the rising time between two defined points in the column using a stopwatch and a high-speed camera (Photron AS1, sigma 105 mm macroscopic lens). It is recommended to set the starting point at a minimum of 50 mm from the tip of the nozzle to ensure the droplet has reached a constant rise velocity [1]. Each measurement was repeated at least three times. Mass transfer contact time was defined as the residence time which includes the formation time as well as the rising time.

To study the effect of Co concentration in the aqueous phase on mass transfer, fresh IL was dispersed into various column lengths containing different Co 0.02, 0.08, 0.17, 0.25, and 0.34 M (1, 5, 10, 15, 20 g/L) and equal Na concentration in g/L from their corresponding chloride salts. On the other hand, the effect of IL concentration was studied using pre-loaded IL obtained by equilibrating fresh IL with aqueous phase containing 0.08, 0.17 and 0.25 M (5, 10 and 15 g/L) Co and equal concentration of Na in g/L from their corresponding chloride salts. Then the pre-loaded IL was injected into the 1.14 m column containing 0.08 M Co (5 g/L) and equal concentration of Na in g/L. Another set of experiments was done by pre-loading fresh IL with 0.08 M Co (5 g/L) and injecting it into columns containing 0.08, 0.17, 0.25, 0.34 and 0.42 M Co (5, 10, 15, 20 and 25 g/L) and equal concentration of Na in g/L to test the effect of pre-loading on extraction rate. ILs was preloaded via mixing the aqueous phase with equal volume of water-saturated $[P_{888}][Oleate]$ (around 10 wt. % water) for 10 min at 40 rpm and centrifuged (3750 rpm; 10 min, 22°C) in an Allegra X-12R Centrifuge of Beckman Coulter.

The effect of droplet size was investigated using an aqueous phase containing 0.02 M Co (1g/L) and equal concentration of Na in g/L. All experiments were performed at room temperature unless stated otherwise. Three samples of the loaded IL were collected at the top of the column in each run, measurements and analysis was conducted as mentioned above. A specific cleaning procedure was performed following each run to avoid contamination of the system.

Figure 5.2: Experimental setup for Co extraction measurements by single rising droplets.

5.3.3 BACK EXTRACTION (REGENERATION)

Back extraction experiments were performed on batch scale as well as using the single droplet extraction column. In batch experiments, 5 ml preloaded $[P_{888}][Oleate]$ with 0.36 M Co (21 g/L) was regenerated using an equal volume of Milli-Q water. Two types of experiments were conducted. In each experiment, 5 ml Milli-Q water mixed with 5 ml pre-loaded IL with 0.36 M Co (21 g/L) and the total regeneration time in both experiments was 2 minutes. The regeneration process was performed either in one stage for the duration of 2 min (A) or in two stages of 1 min each and 30 min in between with both phases completely separated (B).

Using the single droplet extraction column, the back-extraction experiments were performed following the same procedure applied for the extraction. These experiments were conducted by first pre-loading the fresh IL with 0.34 M Co (20 g/L) and then injecting a fixed volume of this pre-loaded IL into the column containing 1 M NaCl solution (25 g/L Na) to create the same environment for the transfer of Co as in the extraction experiments.

All back-extraction experiments were performed at room temperature and in duplicate. At the end of each experiment, the concentration of Co in the (initially Co-free) aqueous

phase was measured since the decrease of Co concentration in the IL droplet was negligible. Measurements and analysis were conducted as mentioned above.

5.4 RESULTS AND DISCUSSION

5.4.1 MODELLING MASS TRANSFER IN LLX

5.4.1.1 CONVENTIONAL MASS TRANSFER CORRELATIONS AND MODELS

In this study a single droplet extraction column, where a single droplet is moving in a stationary ambient phase, was used to avoid the complexity involved in the design of multiphase dispersed systems [9]. This provides a method to investigate the extraction behavior, to measure the mass transfer coefficient and to determine the rate limiting step. Mass transfer of a soluble component into or out of a droplet is classified based on the value of j as either external ($j \gg 1$), internal ($j \ll 1$) or a conjugated problem ($j \approx 1$) [1, 9, 24]. j is defined in Eq. (5.21):

$$j = D \sqrt{\frac{D_i^d}{D_i^c}} \quad (5.21)$$

j is evaluated using (1) variable D assuming that all CoCl_2 in the dispersed phase is free, and (2) constant m assuming that the total CoCl_2 in the IL phase includes both the free and the part complexed with IL (Table 5.1). For the range of the studied Co concentrations, the values of j are close to 1, which indicates that the studied system encounters a conjugated problem where the resistance against mass transfer resides in both the continuous and dispersed phase. During the extraction of Co, the IL droplet exhibits internal circulation behaviour while rising in the single droplet extraction column as has been visually observed (Figure 5.3).

Table 5.1: Parameters employed in Eq. (5.21). The values of D are obtained directly from the extraction isotherm while m is obtained by fitting the extraction isotherm according to Eq. (5.5) as shown in Chapter 4. Diffusivity of Co in the continuous phase is obtained from literature. The diffusivity of CoCl_2 in the dispersed phase is calculated using the Wilke Chang equation as shown in Chapter 4.

Parameters	Values
Distribution coefficient (D)	2-9
Partitioning coefficient (m)	0.9
Diffusivity of Co in the continuous phase (D_i^c)	$1.29 \times 10^{-9} \text{ m}^2/\text{sec}^2$
Diffusivity of CoCl_2 in the dispersed phase (D_i^d)	$4.12 \times 10^{-11} \text{ m}^2/\text{sec}^2$

Figure 5.3: Observed internal circulation within a single IL droplet hanging at the tip of the needle (panel A and B) or rising (panel C) in a single droplet extraction column at different contact times and Co concentrations in the aqueous phase (0.08, 0.17 or 0.34 M Co). Note: the higher the Co concentration in the feed or in the IL, the darker purple the droplet.

Therefore, both the continuous and dispersed phase mass transfer coefficient are calculated using internal circulation models and correlations defined as the following [11]:

1. Continuous phase (internal circulation droplet), the following Sherwood relation was used:

$$Sh_c = 0.6Pe_c^{0.5} \quad (5.22)$$

2. Dispersed phase (Kronig-Brink), the following expression for the mass transfer coefficient in the dispersed phase was used:

$$k_d = -\frac{d}{6t} \ln \left[\frac{3}{8} \sum_{n=1}^{\infty} B_n^2 \exp \left\{ -\frac{64\lambda_n D_i^d t}{d^2} \right\} \right] \quad (5.23)$$

Table 5.2: Eigen-values λ_n and the values of the coefficient B_n used in the model of Kronig-Brink Eq. (5.23) [25, 26].

n	1	2	3	4	5	6	7
B_n	1.31	0.583	0.391	0.35	0.28	0.22	0.16
λ_n	1.60	8.62	21.3	38.5	63.0	89.8	123.8

The continuous and dispersed phase mass transfer coefficients are found to be $k_c = 8.6 \times 10^{-5} - 1.0 \times 10^{-4}$ m/sec and $k_d = 1.8 \times 10^{-5} - 1.2 \times 10^{-4}$ m/sec depending on both droplet diameter and contact time as listed in Table 5.A.1 (Appendix 5.A). Figure 5.4 compares experimental Co uptake using $[P_{888}][\text{Oleate}]$ as function of contact time and droplet diameter for different Co concentrations in the continuous phase with those predicted by the two-film theory where k_c and k_d are calculated according to Eqs. (5.22) and (5.23) respectively. The measured Co uptake (Figure 5.4.A) was always lower than those predicted by the mass transfer model in the case of implementing a distribution coefficient (D) as shown in Eqs. (5.13 - 5.16), while assuming that all Co that is taken up remains in its free form (CoCl_2). The MSE for this case is 1.9×10^{-3} .

Using the partitioning coefficient m instead in Eqs. (5.2) and (5.6), assuming that there is a reaction but it is slow relative to the mass transfer in the time frame of the extraction, improves the prediction of Co uptake and reduces the MSE to 7.8×10^{-5} (Figure 5.4.B). This emphasizes, at least for the system studied here, the importance of using m in the two-film theory in case of having a chemical reaction implying that the extracted metal can be present in more than one form in the solvent. Note in Figure 5.4.B that the model prediction starts to deviate from the experimental data at longer contact time and higher Co concentrations. More specifically the model over-predicts at short contact time and higher Co concentrations, whereas it under-predicts at longer contact time. In the literature, the deviation of the mass transfer coefficient from the value predicted by internal circulation models and correlations is attributed to surface instability (Marangoni effect) [18, 27]. Wang et. al., showed that the measured extraction fraction for the solute transferred from a hanging droplet (1-hexanol) to the aqueous phase agreed quite well with those predicted by the Kronig-Brink model at low solute concentration [28]. At high solute concentration and longer contact time, the Kronig-Brink model predicts the extraction fraction fairly well only if a Marangoni-related parameter is incorporated (i.e., enhancement factor). The incorporated enhancement factor varies based on initial solute concentration and contact time [12, 28]. However, this introduces an extra difficulty in developing a general model that can describe the effect of various operational conditions and hinders the understanding of the extraction mechanism of a LLX system. Figure 5.4 (panel C) shows that the experimental data obtained in feed solutions containing 0.02 and 0.08 M CoCl_2 are relatively insensitive to the droplet diameter ranging between 2.98 and

5.28 mm. Also, in this case the model description based on the partitioning coefficient m is much better than that based on the distribution coefficient D .

Figure 5.4: Effect of contact time on Co uptake for different feed concentrations (0.02–0.34 M Co) compared with the model prediction by Kronig-Brink using either the distribution coefficient D (A) or the partitioning coefficient m (B). Panel C shows the effect of droplet diameter on measured Co uptake and the comparison with the Kronig-Brink, model using either D or m .

5.4.1.2 PARAMETER ESTIMATION

To further understand the mass transfer behaviour of Co in a LLX system and to improve the prediction of Co uptake from literature correlations and, various kinetic models based on the two film theory with and without kinetic reaction were evaluated. In this study, the CV_5 method is applied to (1) discriminate between different rate models, (2) determine the rate-limiting step, and (3) estimate the mass transfer and kinetic parameters. The developed models include mass transfer to and within the IL droplets using a single droplet extraction column as well as the homogenous chemical reaction kinetics and equilibria. Regression and statistical analysis were performed employing cross validation of the different rate models and including all 52 experiments shown in Table 5.A.1 (Appendix 5.A). These experiments involved the effect of contact time, droplet diameter

and the concentration of Co in the continuous and dispersed phase (fresh and pre-loaded IL) on the Co outlet concentration in the IL.

In total, four different extraction models (A-D) were evaluated, accounting for mass transfer with and without homogeneous chemical reaction. The first three models (A-C) without homogeneous chemical reaction are by definition mass transfer-limited. The four cases distinguished in model A are a contribution of both an external and internal mass transfer resistance (A.1-A.4 in Table 5.3) or, alternatively, either only an external mass transfer resistance (B) or only an internal mass transfer resistance (C). The last model investigated include homogeneous chemical reaction (D), in this particular case between the CoCl_2 salt and the IL. In this case, the total resistance is a combination of a mass transfer component and a reaction kinetics component. Ignoring mass transfer resistance altogether is not discussed in this study because the total Co uptake in all experiments is much lower than the equilibrium concentration ($C_{\text{CoCl}_2}^{\text{d}}$).

Table 5.3 shows the fitted parameters, regression values and statistical analysis for each of the four models. For the first three models, A, B and C, i.e., describing extraction in the absence of a chemical reaction, Figure 5.5. compares the experimental and predicted Co uptake. These parity plots show that the results of the models are in good agreement with the experimental data obtained under different operating conditions, over the entire external Co concentration range and using either fresh (blue) or pre-loaded IL (red). Employing k_c and k_d in model A, shows the equal contribution of both an external and internal mass transfer resistance which is in line with the prediction of Eq. (5.21). Statistical analysis presented in Table 5.3 shows that k_c and k_d are cross correlated where $K_{cc}=0.5$. To reduce the cross-correlation value, model A has been re-evaluated using Sh_c and k_d as fitting parameters (A.2) or k_c and Sh_d as fitting parameters (A.3), to account for the effect of droplet diameter and the diffusion coefficient in each phase. Sh_c and Sh_d are defined according to:

$$Sh_c = \frac{k_c d}{D_i^c} \quad (5.24)$$

$$Sh_d = \frac{k_d d}{D_i^d} \quad (5.25)$$

Including Sh numbers in model A.2 and A.3 reduces the cross-correlation values from 0.5 to 0.002 and 0.19 respectively while all other statistical parameters remains unchanged as shown in Table 5.3. However, the system does not encounter a conjugated problem anymore and the resistance against mass transfer resides in either the continuous or the dispersed phase depending on where Sh is applied. Employing Sh_c and Sh_d in model

A.4, shows that the mass transfer resides in the continuous phase. However, statistical analysis shows that Sh_c and Sh_d are cross correlated like k_c and k_d used in model A.1 where $K_{cc}=0.5$. To clarify the effect of the mass transfer resistance in each phase, models B and C are employed where the fitting parameter is either Sh_c or Sh_d . As evident from the Sh_c value in Table 5.3, ignoring the internal mass transfer resistance (case B) hardly affects the outcome compared to that obtained in model A.2. This conclusion is confirmed by the statistical analysis, at least regarding the values of CV_5 and MSE_{best} . On the other hand, ignoring the external mass transfer resistance (case C) reduces the predicting capability outside the training set compared to model A.3, reflecting CV_5 increases from 5.8×10^{-5} to 17.3×10^{-5} . Even though both models B and C provide a comparable fitting ability over the total dataset as evident from the MSE_{best} values in Table 5.3 and parity plots in Figure 5.5 panel B and C. Additionally, the model based on the external mass transfer resistance only (model B) provides the lowest $\sigma_{p,avg}$ which is 3.5 %. This means that when a completely new dataset is considered, the fitted value of the external mass transfer resistance would have a deviation of 3.5 %.

Then, the effect of adding homogenous chemical reaction to the mass transfer is examined for the extraction process as shown in Figure 5.6. The values of the partitioning coefficient m and the equilibrium constants K_{eq} for the homogeneous reactions used in this model are $m = 0.9$ and $K_{eq} = 15$. These parameters are obtained from fitting the isotherm data following the stoichiometry discussed in Chapter 4. Statistical analysis listed in Table 5.3 reveals that the model including both mass transfer and chemical reaction has the lowest CV_5 and MSE_{best} . On the other hand, standard deviation shows a huge variation in the fitted parameters mainly k_r ($3.3 \times 10^{-4} - 8.1 \text{ M}^{-2} \text{ sec}^{-1}$).

Table 5.3: The best fitting parameters out of the five runs based on MSE_{best} obtained for the applied different models developed using CV_5 method. The last five column on the right-hand side listed the regression and statistical analysis of the fitted kinetics models.

Model	Fitting Parameters					Statistical analysis				
	k_c [m/sec]	Sh_c	k_d [m/sec]	Sh_d	k_r [M ⁻² sec ⁻¹]	CV_5	MSE_{best}	$\sigma_{p,avg}$ (%)	N_p	K_{cc}
A. External & internal mass transfer										
1. Using k_c and k_d	1.6×10^{-5}	$4.8 \times 10^{-1*}$	4.5×10^{-5}	$4.1 \times 10^{-3*}$	-	6.0×10^{-5}	5.4×10^{-5}	139.5	2	0.50
2. Using Sh_c and k_d	$1.1 \times 10^{-5*}$	3.2×10^{-1}	3.3×10^{-1}	$3.0 \times 10^{-9*}$	-	5.8×10^{-5}	5.2×10^{-5}	72.0	2	0.002
3. Using k_c and Sh_d	9.7×10^{-2}	$2.9 \times 10^{-5*}$	$1.2 \times 10^{-5*}$	1.1×10^{-3}	-	5.8×10^{-5}	5.2×10^{-5}	248.4	2	0.19
4. Using Sh_c and Sh_d	$1.1 \times 10^{-5*}$	3.2×10^{-1}	4.2×10^{-3}	3.9×10^{-5}	-	5.7×10^{-5}	5.2×10^{-5}	38.3	2	0.5
B. Only external mass transfer Sh_c	$1.1 \times 10^{-5*}$	3.2×10^{-1}	-	-	-	5.7×10^{-5}	5.2×10^{-5}	3.5	1	-
C. Only internal mass transfer Sh_d	-	-	$1.2 \times 10^{-5*}$	1.1×10^{-3}	-	17.3×10^{-5}	5.2×10^{-5}	20.9	1	-
D. Mass transfer & reaction	$1.0 \times 10^{-5*}$	3.0×10^{-1}	5.0×10^{-1}	$4.6 \times 10^{-9*}$	2.5×10^{-1}	4.8×10^{-5}	4.8×10^{-5}	481.7	3	0.36

* k_c , k_d , Sh_c and Sh_d are calculated from the corresponding fitting parameters using the average droplet diameter (i.e., $d=3.8$ mm) and the diffusion coefficients given in Table 5.1.

Figure 5.5: Parity plots of Co uptake and concentration profile at the liquid-liquid interface where the resistance against mass transfer resides in A) both the continuous and dispersed phase B) continuous phase C) dispersed phase.

Figure 5.6: Parity plots of Co uptake and concentration profile at the liquid-liquid interface for mass transfer with chemical reaction.

A high $\sigma_{p,avg}$ value indicates that each of the five runs resulted in a different set of parameters, with each set of parameters still fitting with the experimental dataset. Thus, it is reasonable to conclude that models with higher $\sigma_{p,avg}$ values- although are just as good at fitting experimental data as models with lower values- don't necessarily physically reflect what is being modelled. Therefore, the lower value of $\sigma_{p,avg}$ for model B indicates that the model has a more accurate physical description [19]. The evidence supporting this conclusion is two-fold. First, considering internal mass transport only (model C) increases the CV_5 values with a factor 3. Secondly, adding reaction kinetics to the model description (model D) hardly lowers the CV_5 and MSE_{best} values compared to those models based exclusively on mass transport (models A and B). The low effect of internal mass transfer resistance on Co uptake could be related to the internal circulation that is clearly visually observed during uptake in the extraction column as shown in Figure 5.3.

Figure 5.7 compares experimental Co uptake using $[P_{888}][Oleate]$ as function of contact time for different Co concentrations in the continuous phase with those predicted by the two-film theory using the fitting parameter obtained in model B. The obtained fitting parameter (Sh_c) provides a better prediction of Co uptake even at long contact time and high Co concentration in the continuous phase compared to those obtained using an internal circulation model and correlations from literature as presented in Figure 5.4 (panel B). The value of Sh_c obtained using model B equals 32 which is lower than the value calculated using a literature correlation (Eq. (5.22)) where Sh_c ranges between 251 and 307.

Figure 5.7: Effect of contact time on Co uptake for different feed concentrations (0.02-0.34 M Co) compared with the model prediction based on external mass transfer resistance only (Model B).

5.4.1.3 ACTIVATION ENERGY

The determination of the activation energy is a method to distinguish between a process limited by either mass transfer or reaction kinetics. It is reported that an extraction process is diffusion-limited when the activation energy falls in the range 8-24 kJ/mol. On the other hand, the homogenous reactions contributes to the rate once it exceeds 200 kJ/mol [29]. In order to identify the rate-limiting step during Co extraction by $[P_{888}][Oleate]$, we applied an Arrhenius plot analysis [6, 30, 31]. The temperature effect on the extraction rate controlled by mass transport is less pronounced than that of a process controlled by a chemical reaction [30]. Figure 5.8 shows the influence of temperature on the extraction rate of Co using $[P_{888}][Oleate]$ in the range of 295-353 K (Appendix 5.C). A linear correlation between $\ln dC_{CoCl_2}/dt$ and $1/T$ is obtained where the slope represents $-E_a/R$ according to Arrhenius equation:

$$k_r = A e^{\frac{-E_a}{RT}} \quad (5.26)$$

The activation energy is found to be 24 kJ/mol, a value hinting in the direction of mass transfer limitation which is in line with the conclusion obtained using the model and statistical analysis discussed above.

Figure 5.8: An Arrhenius plot to show the effect of temperature on the extraction rate of Co using $[P_{888}][\text{Oleate}]$. Co concentration in continuous phase is 0.34 M.

5.4.2 BACK EXTRACTION

Another important element in this study is understanding the back-extraction mechanism which is usually ignored in most studies. An earlier study by Othman et al., emphasized already the necessity of selecting the right regeneration solution and understanding its behaviour since the regeneration of the IL and the finally obtained product are key drivers for any liquid-liquid extraction process [7]. In order to investigate the back extraction, experiments were performed using $[P_{888}][\text{Oleate}]$ preloaded with 0.34 M Co. This preloaded IL was regenerated using a 1 M NaCl solution in the 1 m single droplet column. In an extraction system completely dominated by mass transfer, extraction and back-extraction are expected to be symmetrical processes, i.e., the calculated overall mass transfer coefficient in either direction should be the same. This hypothesis was tested by measuring the Co back extraction from IL droplets pre-loaded with Co. The measured Co in the aqueous phase was compared with the calculated concentration using the mass transfer coefficient previously derived from the extraction data. The measured concentration of Co in the aqueous phase after regeneration is found to be 0.15 mM using a 1 M NaCl solution in the column which is almost six times lower than the predicted value (i.e., 0.87 mM) assuming that back extraction is only limited by external mass transfer resistance (Table 5.3). This drop in the measured back-extraction rate could be related to the change of the physical properties of the IL after being complexed with the extracted Co salt. For example, the viscosity of the loaded IL shows an exponential increase as a function of the Co uptake where it increases from 0.13 Pa.sec in fresh IL to 0.14, 0.23 and 0.34 Pa.sec in IL loaded with 0.02, 0.17 and 0.27 M CoCl_2 respectively. This increment in viscosity of the loaded IL reduces the diffusivity of Co within the IL and hinders the internal circulation observed during extraction experiments. To estimate this effect, correlations applicable to rigid, stagnant spheres, not showing any internal circulation are applied to calculate the external and internal mass transfer coefficients using the adjusted diffusivity

coefficient based on the viscosity of the loaded IL which is $1.3 \times 10^{-11} \text{ m/sec}^2$ as calculate in Chapter 4. The mass transfer correlations are defined as the following:

For the continuous phase (stagnant droplets):

$$Sh_c = 2 + 0.66Re^{0.5}Sc_c^{0.3} \quad (5.27)$$

For the disperse phase (Newman):

$$k_d = -\frac{d}{6t} \ln \left[\frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -\frac{4n^2 \pi^2 D_i^d t}{d^2} \right\} \right] \quad (5.28)$$

The rate model, using Eqs. (5.27) and (5.28) for k_c and k_d respectively valid for a stagnant droplet, provides a better prediction for the Co concentration in the aqueous phase after back-extraction as shown in Table 5.4 (i.e., 0.15 mM compared to the experimental concentration of 0.15 mM). It is worth noting that during back extraction the internal mass transfer resistance becomes dominant where $k_d = 2.8 \times 10^{-6} \text{ m/sec}$ and $k_c = 3.6 \times 10^{-5} \text{ m/sec}$ ($Sh_c = 101$).

Table 5.4: Comparing the measured Co concentration after back extraction with the predicted values obtained using mass transfer coefficient derived from the extraction data and mass transfer correlations for stagnant droplet.

Modelling Free Co	Pre-loaded Co in IL [M]	Exp. regenerated Co [mM]	Model regenerated Co [mM]
Parameter estimation from extraction			0.87
Stagnant droplet correlations	0.34	0.15	0.15

Back extraction experiments were also performed on batch scale, to verify whether the effect of a possible decomplexation reaction becomes more apparent at longer time scales. These experiments were performed using preloaded $[P_{888}][\text{Oleate}]$ with 0.36 M Co. The preloaded IL was regenerated using an equal volume of Milli-Q water (in the absence of NaCl to avoid any extra effect). The total regeneration time in both experiments was 2 minutes where the regeneration process was performed A) in one stage for the duration of 2 min, and B) in two stages each of 1 min allowing 30 min in between. This time delay is introduced to give extra time for decomplexation and formation of free Co that can be transferred from the organic to the aqueous phase during the second stage. If the back extraction would be continuously dominated by the external mass transfer, a time delay should have no influence on the amount of regenerated Co. As shown in Table 5.5, the introduction of a 30 min time delay resulted in 13% extra Co transfer from IL to the

aqueous phase. Given an estimated experimental error of ± 0.4 mM, the effect seems significant. On the other hand, the 13% increase remains a rather marginal effect and does not justify the conclusion that the decomplexation reaction is the rate-limiting step during back extraction.

Table 5.5: Effect of time delay on the concentration the Co in the aqueous phase after regeneration.

Exp	Number of stages	Stage duration [min]	Time delay [min]	Aqueous phase Co [mM]
Exp_A	1	2	-	40
Exp_B	2	1	30	46

5.5 CONCLUSIONS

Present study focusses on the single droplet extraction of Co from an aqueous solution using IL $[P_{888}][Oleate]$ droplets. The analysis investigates the mass transfer in the forward and back extraction with and without a chemical reaction and determines the rate limiting step. The results reveal that a mass transfer model with just a single fitting parameter, Sh_c , adequately describes the extraction of Co for the whole data set with most of the experimental data predicted within $\pm 30\%$, regardless of the initial solute concentration in the continuous and dispersed phase, contact times or droplet diameters. Adding a chemical reaction to the model does not improve the predictions significantly. This is in line with the measured low activation energy of the extraction rate (E_a is 24 kJ/mol).

Unfortunately, the parameters determined from extraction experiments are not able to describe the back extraction of Co. This is maybe due to a change of the physical properties (mainly increased viscosity) of the IL after being complexed with the extracted Co. However, using correlations applicable to rigid, stagnant spheres to calculate the external and internal mass transfer coefficients provides a much better prediction for the Co concentration in the aqueous phase after back-extraction.

APPENDIX 5.A

Table 5.A.1: The operational condition of the all the experiments performed using single droplet extraction column including column length, initial Co concentration in the feed and IL, initial concentration of IL, residence time and droplet diameter.

ID	Column length [m]	$C_{Co,in}^c$ [mol/L]	$C_{CoCl_2-Total,in}^d$ [mol/L]	C_{IL}^d [mol/L]	Residence time [sec]	Droplet diameter [mm]
Exp_01	0.02	0.02	0.00	1.06	2.3	4.1
Exp_02	0.02	0.08	0.00	1.06	2.1	4.0
Exp_03	0.02	0.17	0.00	1.06	1.9	3.8
Exp_04	0.02	0.25	0.00	1.06	1.7	3.6
Exp_05	0.02	0.34	0.00	1.06	1.5	3.5
Exp_06	0.29	0.02	0.00	1.06	5.8	4.1
Exp_07	0.29	0.08	0.00	1.06	5.2	4.0
Exp_08	0.29	0.17	0.00	1.06	5.0	3.8
Exp_09	0.29	0.25	0.00	1.06	4.6	3.6
Exp_10	0.29	0.34	0.00	1.06	4.4	3.5
Exp_11	0.64	0.02	0.00	1.06	10.1	4.1
Exp_12	0.64	0.08	0.00	1.06	9.4	4.0
Exp_13	0.64	0.17	0.00	1.06	9.0	3.8
Exp_14	0.64	0.25	0.00	1.06	8.4	3.6
Exp_15	0.64	0.34	0.00	1.06	8.1	3.5
Exp_16	1.14	0.02	0.00	1.06	16.7	4.1
Exp_17	1.14	0.08	0.00	1.06	15.3	4.0
Exp_18	1.14	0.17	0.00	1.06	14.7	3.8
Exp_19	1.14	0.25	0.00	1.06	13.9	3.6
Exp_20	1.14	0.34	0.00	1.06	13.4	3.5
Exp_21	1.47	0.02	0.00	1.06	21.0	4.1
Exp_22	1.47	0.08	0.00	1.06	19.2	4.0
Exp_23	1.47	0.17	0.00	1.06	18.5	3.8
Exp_24	1.47	0.25	0.00	1.06	17.5	3.6
Exp_25	1.47	0.34	0.00	1.06	17.0	3.5
Exp_26	0.64	0.02	0.00	1.06	9.3	3.0
Exp_27	0.64	0.02	0.00	1.06	9.4	3.1
Exp_28	0.64	0.02	0.00	1.06	10.1	4.0
Exp_29	0.64	0.02	0.00	1.06	10.3	4.1
Exp_30	0.64	0.02	0.00	1.06	10.4	4.3
Exp_31	1.14	0.02	0.00	1.06	16.0	3.0
Exp_32	1.14	0.02	0.00	1.06	16.0	3.1
Exp_33	1.14	0.02	0.00	1.06	16.5	4.0
Exp_34	1.14	0.02	0.00	1.06	16.7	4.1
Exp_35	1.14	0.02	0.00	1.06	16.7	4.3
Exp_36	1.14	0.02	0.00	1.06	17.3	4.8
Exp_37	1.14	0.02	0.00	1.06	18.2	5.3

Exp_38	0.64	0.08	0.00	1.06	9.3	3.0
Exp_39	0.64	0.08	0.00	1.06	9.4	3.2
Exp_40	0.64	0.08	0.00	1.06	10.0	3.9
Exp_41	0.64	0.08	0.00	1.06	10.1	4.0
Exp_42	0.64	0.08	0.00	1.06	10.4	4.2
Exp_43	0.64	0.08	0.00	1.06	11.8	5.1
Exp_44	1.14	0.08	0.08	0.89	15.5	3.8
Exp_45	1.14	0.17	0.08	0.89	14.6	3.7
Exp_46	1.14	0.25	0.08	0.89	14.3	3.6
Exp_47	1.14	0.34	0.08	0.89	13.4	3.5
Exp_48	1.14	0.42	0.08	0.89	13.0	3.4
Exp_49	1.14	0.08	0.00	1.06	15.0	4.0
Exp_50	1.14	0.08	0.08	0.89	15.3	3.8
Exp_51	1.14	0.08	0.16	0.74	15.6	3.8
Exp_52	1.14	0.08	0.22	0.63	16.3	3.7

APPENDIX 5.B

To test the robustness of the model based on the external mass transfer resistance fitted in terms of Sh_c , a sensitivity analysis is performed by varying 1) the internal mass transfer coefficient k_d from 1×10^{-6} to 1×10^{-4} m/sec, 2) the partitioning coefficient m from 0.5 to 10, and 3) the fitted data set (fitting data with Co uptake <0.05 M). These scenarios provide almost the same value for Sh_c and has no effect on the fitting ability and the prediction capability as shown in Table 5.B.1. The obtained fitted Sh_c is lower than that obtained using literature correlation where Sh_c ranging between 250.7 and 307.4.

Table 5.B.1: sensitivity analysis applied on external and internal mass transfer model.

Variables	Used values/ data set	Sh_c	MSE	CV_s	MSE_{best}
k_d	1.0×10^{-6}	32.4	5.9×10^{-5}	5.7×10^{-5}	5.2×10^{-5}
	1.0×10^{-4}	37.0	5.9×10^{-5}	5.8×10^{-5}	5.2×10^{-5}
m	0.5	38.1	6.0×10^{-5}	5.8×10^{-5}	5.2×10^{-5}
	10	28.1	6.0×10^{-5}	5.8×10^{-5}	5.4×10^{-5}
Data set	Co uptake <0.05 M	35.9	1.3×10^{-5}	2.4×10^{-5}	6.1×10^{-5}

APPENDIX 5.C

Table 5.C.1: The operational conditions of experiments performed at different temperatures in single droplet extraction column (0.64 m) including column length, temperature, initial Co concentration in the feed, residence time and droplet diameter. Last two columns list Co uptake and uptake rate respectively.

ID	Temperature [K]	$C_{Co,in}^c$ [mol/L]	Residence time [sec]	Droplet diameter [mm]	$C_{CoCl_2,Total}^d$ [mol/L]	$dC_{CoCl_2,Total}^d/dt$ [M/sec]
Exp_53	296	0.34	8.1	3.5	0.06	0.007
Exp_54	323	0.34	8.3	3.5	0.18	0.022
Exp_55	353	0.34	8.5	3.8	0.29	0.034

Nomenclature

Symbols	Description	Unit
a	Specific interfacial area $\left(\frac{6}{d}\right)$	m^2/m^3
B_n	n^{th} coefficient in the equation of Kronig-Brink	-
C	Concentration	M
C_{Co}	Solute concentration free (Co)	M
C_{CoCl_2}	Solute concentration free (CoCl_2)	M
$C_{\text{CoCl}_2\text{-IL}}$	Solute concentration complexed with IL	M
$C_{\text{CoCl}_2,\text{Total}}$	Total Solute concentration (free and complexed with IL)	M
C_{IL}	IL concentration free	M
$C_{\text{IL},\text{total}}$	IL concentration both free and complexed with CoCl_2	M
CC	Cross correlation matrix	-
CV_5	5-fold cross validation	-
D	Distribution coefficient	-
D_i	Diffusion coefficient	m^2/sec or cm^2/s
d	Droplet diameter	m
E_a	Activation energy	kJ/mol
J	Flux	mol/m^2
K	Overall mass transfer coefficient	m/sec
k	Partial mass transfer coefficient	m/sec
K_{cc}	Average correlation value of the cross-correlation matrix	-
K_{eq}	Equilibrium constant (Homogenous reaction)	-
$k_{\text{eq,int}}$	Equilibrium constant (Heterogenous reaction)	-
k_r	Reaction rate constant (Homogenous reaction)	$\text{M}^{-2}\text{sec}^{-1}$
$k_{\ddagger}$	Forward and backward reaction rate constant (Heterogenous reaction)	$\text{M}^{-2}\text{sec}^{-1}$
m	Partition coefficient	-
MSE	Mean square error	-
n	Indices	-

N	Number of experiments	-
N _p	Number of parameters	-
P _i	Fitted parameter of the MSE _{best} fit	-
Pe	Peclet number $\left(\frac{du}{D}\right)$	-
R	Gas constant 8.31446	J/mol K
r	Reaction rate	M/sec
Re	Reynolds number $\left(\frac{\rho u d}{\mu}\right)$	-
Sc	Schmidt number $\left(\frac{\mu}{\rho D_i}\right)$	-
Sh	Sherwood number $\left(\frac{k d}{D_i}\right)$	-
T	Temperature	K
t	Residence time	sec
u	Slip velocity	m/sec
V	Droplet volume	m ³
wt.	weight fraction	%

Greek letters

λ_n	n th Eigen values in the equation of Kronig-Brink	-
ρ	Density	kg/m ³
σ_{P_i}	Standard deviation of each parameter over the 5 fits	%
$\sigma_{P,avg}$	Average standard deviation of a model over 5 fits	%
μ	Viscosity	Pa sec

κ	Viscosity ratio $\left(\frac{\mu_d}{\mu_c}\right)$	
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Superscripts

c	Continuous phase	
d	Dispersed phase	
n	Number of anions	
*	Equilibrium	

Subscripts

c	Continuous phase
d	Dispersed phase
in	Inlet
int	Interface
n	Number of anions
exp	Experimental

Abbreviations

Co	Cobalt
Exp	Experimental
IL	Ionic liquid
LLX	Liquid-liquid extraction

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CHAPTER 6

COBALT EXTRACTION IN A BENCH SCALE RECIPROCATING PLATE COLUMN

Failure is not the opposite of success it is part of success

Debbie Gregory

ABSTRACT

Liquid-liquid extraction was applied to extract Co from an aqueous stream using the ionic liquid $[P_{8888}][Oleate]$ in a 5/8" diameter KARR® reciprocating plate column. It was necessary to dilute the ionic liquid with n-dodecane to create solvent droplets and to add isopropyl alcohol as demulsifying agent. The loaded solvent (ionic liquid + n-dodecane + isopropyl alcohol) was regenerated batch-wise with 1 M Na_2CO_3 . It was found that an increased column capacity had no significant effect on the extraction efficiency, defined as $(1 - C_{out}/C_{in})$. The lack of effect is ascribed to a balance between the positive effect of increased interfacial area resulting from a higher hold up, and the negative effect of reduced contact time. Increasing the agitation rate from 150 to 250 SPM improved the extraction performance from 36% to 48%, which is close to the performance of one equilibrium stage. This improvement in the extraction efficiency is attributed to the increase of interfacial area available for mass transfer resulting from a smaller droplet size and higher holdup. A mathematical model, including literature correlations for mass transfer, holdup and droplet diameter, was developed. The model results were compared with experimental data obtained in this study as well as one study found in literature as reported by others. The model can predict experimentally observed trends (e.g. efficiency as a function of capacity) and the absolute extraction performance within an AARE of less than 20%.

6.1 INTRODUCTION

In this chapter, a first step is reported regarding the scale-up of Co extraction using [P₈₈₈₈][Oleate]. Earlier studies showed the performance of Co extraction using IL in a continuous mode in mixer-settlers [1, 2]. Despite the advantages of mixer settlers, such as simplicity of design and ease of upscaling, extraction columns are preferred in separation processes. This is because extraction columns provide more theoretical stages at a lower footprint compared to a maximum of one theoretical stage per mixer-settler apparatus [3]. Moreover, applying [P₈₈₈₈][oleate] for Co extraction in a mixer-settler resulted after a few cycles in the formation of a stable emulsion which limits the applicability of the process.

The design of extraction columns requires optimization regarding internal material properties, agitator diameter, free cross-sectional area, flow rate of dispersed and continuous phase and mass transfer area [4, 5]. In this study the KARR® reciprocating plate column was selected as a counter-current mechanically agitated column which theoretically should be able to handle emulsifying systems such as [P₈₈₈₈][Oleate]. Reciprocating plates enhances mass transfer by the creation of (small) droplets and accordingly an increase of the mass transfer area. The use of a KARR® column in combination with an ionic liquids has previously been reported by Yung et al., for the extraction of phenol from water [6].

In this study we investigated the influence of operating variables, including the frequency of agitation and the flow rates of the solvent and aqueous phase, on the column performance. Experiments were performed to investigate the extent to which the solvent to feed ratio affects the hydrodynamic performance of the unit without causing flooding. A model was developed to predict the mass transfer performance for the extraction of Co from the aqueous phase into the IL, including the effect of axial dispersion in the continuous phase. The experimental results of the present study along with those reported in literature have been used to test the validity of the developed model for the considered 5/8" and 2" diameter KARR® extraction columns [7].

6.2 MODELLING

Earlier studies by Novotny *et al.* (1970), Nemecek and Prochazka (1974) and Prvcic et al., (1989) investigated the importance of axial dispersion (i.e., back-mixing) in the aqueous and dispersed phase in five different organic systems [8-10]. It was found that in general axial dispersion in the continuous phase can be of major importance due to its effect on reducing the driving force for mass transfer. This is mainly a result of the circulatory flow induced by 1) movement of the disc 2) molecular and turbulent diffusion in the axial

direction and 3) channelling and non-uniform velocity distribution across the tower cross section [11]. However, this is only valid for systems with $Pe_a \ll 1$, which is defined as $Pe_a = Hu_c/E_a^c$ [12]. The continuous phase axial dispersion is predicted with the modified version of the Prvcic model, where the values of the parameters were refitted by Stella [10, 13]. Based on the numerical calculation done by Chartres and Korchinsky in 1975, the axial dispersion of the dispersed phase is negligible [14, 15].

In this study a model has been developed assuming 1) steady-state conditions, 2) a negligible radial concentration gradient due to the small column diameter, 3) constant thermo-physical properties over the entire column length, 4) plug flow for the dispersed phase, 5) dispersed flow for the continuous phase, 6) mass transfer that can be described by the two-film model, 7) equilibrium conditions at the interface with the concentrations predicted by the experimentally obtained isotherm and 8) immiscibility of the two phases.

6.2.1 MASS BALANCE

Figure 6.1 shows a schematic representation of (steady-state) mass transfer from the continuous (aqueous) into the dispersed (IL) phase in a KARR[®] column operating under counter-current conditions. The change in cobalt concentration in the two phases along the column length has been modelled by two coupled differential equations. Note that the equation for the continuous phase includes a term accounting for the effect of axial dispersion. The model also includes an algebraic equation (isotherm) that describes the equilibrium concentrations at the interface. This set of equations has been solved over a differential element Δz of the column length. In this system the dispersed phase is fed from the bottom of the column, while the continuous phase is fed from the top of the column.

Figure 6.1: Schematic diagram of the differential axial dispersion model for an extraction column.

For the continuous phase:

$$E_a^c \frac{d^2 C^c}{dz^2} + u_c \frac{dC^c}{dz} - k_c^{c \rightarrow d} a (C^c - C_{int}^c) = 0 \quad (6.1)$$

For the dispersed phase:

$$u_d \frac{dC^d}{dz} - k_d^{c \rightarrow d} a (C_{int}^d - C^d) = 0 \quad (6.2)$$

In this study the value of u_c and u_d are taken both as positive.

Both Co concentrations at the interface are at equilibrium and related by equating the solute flux out of the continuous phase into the dispersed phase as shown in Eq. (6.3):

$$k_c^{c \rightarrow d} a (C^c - C_{int}^c) = k_d^{c \rightarrow d} a (C_{int}^d - C^d) \quad (6.3)$$

The equilibrium correlations between C_{int}^c and C_{int}^d in [mol/m³] are obtained by fitting the isotherm for pure and regenerated solvent (IL and n-dodecane), resulting in Eqs. (6.4) and (6.5) respectively:

For fresh solvent:

$$C_{int}^c = 1.5 \times 10^{-3} (C_{int}^d)^{2.32} \quad (6.4)$$

For the regenerated solvent:

$$C_{int}^c = 9.3 \times 10^{-6} (C_{int}^d)^{3.30} \quad (6.5)$$

This method allows the use of the model for any isotherm defined by the general function as shown in Eq. (6.6):

$$C_{int}^c = f(C_{int}^d) \quad (6.6)$$

These differential and algebraic equations (6.1-6.5) are solved using the following boundary conditions:

For the continuous phase:

$$\frac{dC^c}{dz} = 0|_{z=0} \quad (6.7)$$

$$E_a^c \frac{dC^c}{dz} - u_c (C^c - C_{in}^c) = 0|_{z=H} \quad (6.8)$$

For the dispersed phase:

$$C^d = C_{in}^d|_{z=0} \quad (6.9)$$

Where C_{in}^d is the initial Co concentration in the dispersed phase which equals zero in the case of using fresh solvent, and the initial Co concentration remains in the solvent after regeneration in the case of using regenerated solvent.

Further details including the required correlations and the equations used for parameter calculation such as drop size distribution, dispersed phase holdup, mass transfer and axial dispersion coefficients, as well as MATLAB implementation are presented in Appendix 6.A.

6.2.2 NUMERICAL CODE VERIFICATION

The verification of the numerical code for the developed model is carried out by comparing the model results obtained for a simplified plug flow model for both phases simulated with constant mass transfer coefficients in the continuous and dispersed phase, interfacial area and distribution coefficient, with the analytical solution.

The obtained Co concentration profiles for the continuous and dispersed phase are in full agreement with the analytical solution as discussed in Appendix 6.A. The physical properties of all pure chemicals, characteristic of the extraction column and model parameters are tabulated in Table 6.A.2.

6.2.3 LLX EFFICIENCY

The LLX process is evaluated based on the extraction efficiency, reflecting the actual amount of transferred solute from the continuous to the dispersed phase. The extraction efficiency is defined as follows:

$$\eta_E = \frac{C_{in}^c - C_{out}^c}{C_{in}^c} \times 100 \% \quad (6.10)$$

The Average Absolute Relative Error (AARE) is derived from the difference between predicted and experimental data and is defined as:

$$AARE = \frac{1}{N} \sum_{i=1}^N \frac{|C_{model} - C_{exp}|}{C_{exp}} \times 100 \% \quad (6.11)$$

6.3 EXPERIMENTAL

6.3.1 MATERIALS AND ANALYSIS

Tetraoctylphosphonium bromide (> 95 %) was purchased from IoLiTec; sodium chloride, nitric acid (69 %) and sodium carbonate (>99%) from VWR Chemicals; oleic acid (90 %), perchloric acid (70%), cobalt (II) chloride hexahydrate (98 %), n-Dodecane (>99%) and isopropyl alcohol from Alfa Aesar. MilliQ water ($\geq 18 \text{ M}\Omega\cdot\text{cm}$) was obtained from a Millipore Milli-Q® Biocel, which uses a Qgrade® column. All chemicals were used as purchased, without any further purification. $[\text{P}_{8888}][\text{Oleate}]$ was synthesized according to the procedure described in Chapter 3.

The aqueous phase after each extraction process was analysed using a Perkin Almer Optima 5300 DV inductive coupled plasma optical emission spectrometry (ICP-OES) (detection range: 0.025 - 10 mg/L). The concentration of isopropyl alcohol (IPA) in the aqueous phase was analysed using a High-Pressure Liquid Chromatograph (HPLC) of the Agilent Technologies 1200 series. The organic phase was digested using a Milestone Ethos Easy microwave digester as described in earlier studies [16, 17]. Afterwards, the digested samples were diluted and analysed using the same instruments as used for the analysis of the aqueous phase.

6.3.2 EQUIPMENT: KARR® COLUMN

The mass transfer experiments were carried out in a 5/8" (15.9 mm) internal diameter KARR® column Bench Top Unit (BTU) manufactured by Koch Modular Process System (Figure 6.2). KARR® columns up to 66" diameter have been successfully designed with the scale-up data generated on a 1" diameter pilot column. However, a 1" diameter pilot plant requires the use of 190 and 380 L of feed and solvent, respectively. To reduce the amount of material necessary, a smaller diameter column of 5/8" has been implemented for initial feasibility studies on the counter-current liquid-liquid extraction process. Cusack et al., used the water-acetone toluene system to prove that the 5/8" column has a strong correlation with the 1" and 2" column for capacities of $30 \text{ m}^3/\text{m}^2\text{hr}$ and above [18]. Therefore, under the appropriate operating conditions, the 5/8" diameter column is a good choice to test the liquid-liquid extraction performance for a small amount of solvent. The specifications of the column used in this study are listed in Table 6.1.

Figure 6.2: KARR® Column Bench Top Unit (BTU).

Table 6.1: Column specification.

Parameter	Specification
Column Diameter	15.9 mm
Effective Column Height	60.1 cm
Effective Column Volume	119.6 cm ³
Types of Plates	stainless-steel
Number of Plates	24
Plate Spacing	25.4 mm
Plate Free Area	55%

The BTU consists of a glass-shell column mounted onto a stainless-steel base and support frame. The unit has been designed with an agitator assembly including an air motor, eccentric shaft, push rod, rocker arm and plate stack which is designed to reciprocate up and down as in a typical KARR® column operation. The column consists of 24 stainless-steel evenly spaced plates with free area of approximately 55% mounted on a central shaft. The plate diameter is made as large as possible, to minimize the annular gap between the plates and the column wall. The height of the plate stack is 24" (60.9 cm) with 1" (25.4 mm) plate spacing. The speed of reciprocation is controlled precisely over a range of 100–400 stacks per minute (SPM) with gas flow of air supplied to the air motor. The reciprocating speed was measured by the Sper Scientific 840009 Digital Stroboscope. Aqueous and organic phases are dosed by Diaphragm Metering Pumps (STEPOS 08 S).

6.3.3 PROCEDURE

Mass transfer measurements were performed in the KARR® column using either fresh or regenerated solvent and an aqueous phase containing 5 g/L Co and Na from their corresponding chloride salts. NaCl was used as a salting-out reagents to improve the

extraction efficiency, as demonstrated by Othman et.al., [16]. The organic phase (solvent) was composed of extractant (IL), diluent (n-dodecane) in a 1:2 weight ratio and 5 wt.% IPA. In this investigation, the organic phase was chosen as the phase to be dispersed as it has a higher viscosity and lower density compared to the aqueous phase and, not unimportant, is the more expensive of the two liquids. To study the effect of hydrodynamic behaviour on mass transfer, three different capacities (20, 30 and 38 m³/m²hr), defined as the sum of both flows at a fixed solvent-to-feed ratio that passes through the column cross-sectional area, and agitation rates (150, 200 and 250 SPM) were tested. The time needed to reach steady state was estimated by operating the column for a minimum of five turnovers in the first run after a shutdown period and for a minimum of three turnovers for the following runs. A turnover is defined as the volume of the column divided by the combined flowrates of both feed and solvent. Once the system reached steady state, samples of the raffinate were collected at the bottom of the column, and analysis were conducted as mentioned above.

After each extraction, a batch experiment was performed to regenerate the solvent loaded with Co using 1 M Na₂CO₃. In each experiment, 25 ml aqueous phase of 1 M Na₂CO₃ was mixed with 25 ml of extract for 2 hrs at 40 rpm in a mechanical laboratory agitator loopster digital manufactured by IKA and centrifuged (3750 rpm; 20 min, 22 °C) in an Allegra X-12R Centrifuge manufactured by Beckman Coulter. From that point on, the regenerated solvent was exposed to fresh feed solution for the next extraction cycles in the KARR[®] column. This procedure was repeated for four complete subsequent cycles of extraction and regeneration.

6.4 RESULT AND DISCUSSION

6.4.1 KARR[®] COLUMN OPERATIONAL WINDOW AND PERFORMANCE

To scale up any potential LLX system, it is important to evaluate its hydrodynamic behaviour and mass transfer performance. Therefore, the KARR[®] column has been used to evaluate the applicability of the Co-IL system studied here. Earlier batch-mode studies under shaking conditions and single drop extraction column experiments showed a high Co extraction efficiency using [P₈₈₈₈][oleate] in its pure form. However, using pure IL in the KARR[®] column showed a drastic change in the physical properties of the IL once Co extraction began. The IL without Co formed droplets in the continuous phase, while at the onset of Co extraction, the IL started to stuck to the internal surfaces of the column, possibly due to rather strong adhesion forces between the Co-IL complex and the glass and metal surfaces of the column (Figure 6.3). This interaction hampered droplet formation and with that compromised mass transfer as shown in Table 6.2. The adhesion force might result from the electrostatic interaction between Co ions and the negatively

charged glass surface, due to the dissociation of silanol group [19]. In addition, stainless steel surface is positively charged over the pH range of 2.5-5.0 due to the protonation of the surface hydroxyl groups which may act as adsorption sites for the negatively charged Cl ions [20, 21]. Theoretically, coating the internal glass wall and/or stainless-steel surface with a non-ionic polymer can remedy this problem, given the particular polymer (for instance polystyrene or polypropylene) can withstand the experimental conditions. Batch experiments performed using vials made of these types of polymers show no electrostatic interaction with the loaded IL.

Table 6.2: Cobalt extraction using pure IL in KARR® column at room temperature.

Column capacity [m ³ /m ² hr]	Throughput [ml/min]	S/F	SPM	[Co] _{Feed} [g/L]	[Co] _{Raff} [g/L]	Extraction efficiency [%]
10	33	0.3	60	5	4.19	16

There are four different options to improve the mass transfer performance and hydrodynamic behaviour 1) increasing the agitation rate, 2) decreasing the throughput, 3) increasing the temperature and 4) phase reversing. Increasing the agitation rate up to 80 SPM resulted in a flooded column due to the high viscosity, making this option non-viable. Usually, lowering throughput and accordingly column capacity improves the extraction performance by prolonging the contact time. However, a further decrease in the throughput below a capacity of 10 m³/m² hr makes the process non-feasible since this capacity represents the lower limit of the operational window of an extraction column, apart from the low extraction efficiency as shown in Table 6.2. To reduce the viscosity of the IL, Co extraction was performed at a higher temperature (i.e. 70 °C). However, adhesion forces towards the surfaces of the column were still very strong, preventing droplet formation and solvent dispersion in the feed as shown in Figure 6.3. Therefore, no tangible improvement was found in terms of performance. Reversing the phases, i.e. applying IL as continuous phase and the aqueous solution as dispersed phase, was not considered since the main purpose of this study and potential application is to treat large capacities of water with an as small as possible amount of solvent.

Figure 6.3: Hydrodynamic behaviour of IL at A) 22 °C and B) 70 °C. Note the purple coloured IL sticking to glass surface and metal plate stack.

Since none of the above-mentioned options were viable, an alternative approach was needed to allow operation of the column with this particular IL. Therefore, the diluent n-Dodecane was added to IL because it is completely miscible with the IL, reduces its viscosity and interfacial tension (Table 6.3), has a low volatility and solubility in the aqueous phase (non-polar), and does not influence the extraction efficiency relative to the amount of IL applied (Figure 6.B.1).

Table 6.3: Physical properties of pure IL and IL dissolved in n-dodecane with 1:2 weight ratio including density, viscosity, and interfacial tension.

Parameters	ρ [kg/m ³]	η [mPa.s]	γ [mN/m]
Pure IL	896	133	73
IL+n-dodecane	793	14	45

Different IL to n-dodecane ratios on weight bases were investigated ranging from 1:1 to 1:2 as shown in Figure 6.4. Increasing the amount of n-dodecane resulted in a better hydrodynamic performance and a lower chance of flooding at higher SPM (when other operating parameters were kept constant). In this study, the optimum IL to n-dodecane ratio was found to be 1:2, as discussed in more detail later on in this section.

The main parameters considered in determining the operational window of the 5/8" diameter KARR® column are:

- Capacity: column performance should improve at capacities lower than 30 m³/m²hr due to the long contact time, the high wall effect and reduced axial dispersion [18]. To correlate the efficiency of the column with larger diameter KARR® columns capacities above 30 m³/m²hr should be applied. Three different capacities have been selected

20, 30 and 38 m³/m²hr. The highest capacity possible was dictated by the pump flow rate limit (80 ml/min).

- Strokes Per Minute (SPM): hydrodynamic performance improves with increasing the agitation rate up to a certain point. This is due to the formation of smaller droplets and higher hold-up. However, if the agitation speed is too high, column performance becomes lower due to flooding where the dispersed phase stops flowing counter currently to the continuous phase or back-mixing of the continuous phase [22]. In this study three different agitation rates were examined 150, 200 and 250 SPM.
- Solvent:Feed ratio (S/F): In this study the total solvent consists of both IL and n-dodecane, where the selected S/F volume ratio of 0.58 (i.e., 0.45 on weight ratio) ensures stable column operation at 250 SPM without experiencing flooding or phase inversion. This corresponds to an IL:Feed weight ratio of 0.15 with a mass ratio of 1:2 for IL:n-dodecane in the solvent.

Figure 6.4: Solvent (IL-n-dodecane-IPA): feed volume ratio as function of both weight ratios of IL:n-dodecane and IL:feed. The ratios 1:2.5 and 1:3 are added in case a higher amount of n-dodecane is needed.

The extraction efficiency of Co using fresh IL for different agitation rates and capacities is presented in Figure 6.5. Increasing the agitation speed from 150 SPM to 250 SPM increased the extraction of Co from 23 % to 35% at a capacity of 20 m³/m²hr and from 20 % to 33 % at a capacity of 38 m³/m²hr using fresh solvent. Higher agitation rates increase the holdup and reduces the mean droplet size, due to more severe collisions between the droplets and the reciprocating plates, internal wall and the shaft [23]. This increases the interfacial area available for mass transfer and accordingly the extraction performance. On the other hand, increasing the capacity from 20 m³/m²hr to 38 m³/m²hr showed no significant effect on the extraction of Co which is in line with the predicted values presented in Figure 6.10. This behaviour could be explained by a balance between the positive effect of

increasing flowrates of both phases, leading to a higher holdup and resulting in a larger interfacial area available for mass transfer and the negative effect due to a shorter contact time. This is in line with the analytical solution where parameter E , which is defined as $E = K * a * (m * \tau_c - \tau_d)$, remains constant for different capacities operating at a fixed agitation speed, as tabulated in Table 6.4.

Figure 6.5: Effect of agitation rate (in SPM) and column capacity on Co extraction efficiency using fresh solvent with a fixed S/F volume ratio of 0.58 compared to the extraction efficiency of one equilibrium (Equ) stage. Error bars are based on standard deviations of the population (68% confidence).

Scaling up any potential liquid-liquid extraction system requires successful solvent regeneration without influencing its extraction performance on the long term. In this study, 1 M Na_2CO_3 has been used as regeneration solution to recover the used solvent (IL+n-dodecane) and precipitate the Co in the form of CoCO_3 as end product. However, using regenerated IL in the KARR® column showed the formation of a stable emulsion which made phase separation very difficult. This could be due to the transfer of Na to the IL (exchange with Co) during solvent regeneration and the formation of NaCl which, in turn, enhances emulsion formation [16]. Therefore 5.5 wt.% of IPA was added to the solvent as a demulsifier to ease phase separation. In a previous study, IPA has been employed successfully for Co extraction using methyltriocylammonium chloride [24]. After extraction, the measured concentration of IPA in the raffinate was found to be around 1.3 wt.%. The lost IPA needs to be replenished after each extraction-regeneration cycle to avoid emulsion formation.

Further research regarding the recycling of IPA should be considered, however a preliminary economic analysis showed that the overall process is still profitable due to the high price of the produced Co even without recycling the lost IPA.

Figure 6.6: Co extraction efficiency (blue colour) and initial Co concentration present in the IL at the start of each cycle (red colour) for both fresh and regenerated IL with a S/F volume ratio of 0.58 at different agitation rates and $30 \text{ m}^3/\text{m}^2 \text{ hr}$ capacity compared to the extraction efficiency of one equilibrium stage. Co extraction efficiency of one equilibrium stage of fresh and regenerated solvent is calculated using the Co extraction isotherm belonging to the fresh and the regenerated solvent respectively. Error analysis based on population standard deviation for the extracted and mean standard deviation of the mean for the Co left in IL confidence interval of 68%.

To investigate the stability and performance of the regenerated solvent, four consecutive extraction-regeneration cycles were performed. Figure 6.6 illustrates the extraction efficiency of Co over the four consecutive cycles, which were performed with a capacity of $30 \text{ m}^3/\text{m}^2\text{hr}$ and a S/F volume ratio of 0.58. The regenerated solvent showed higher extraction efficiencies compared to the fresh solvent. The extraction efficiency increased from 20% to 36% at 150 SPM and from 30% to 48% at 250 SPM, which is around 76% of the performance of one equilibrium stage. The results are reported in more detail in Appendix 6.C. This improvement in extraction performance may be related to the switch in extraction mechanism from ion-pair using the fresh solvent to ion-exchange using the regenerated solvent [16]. During ion pair extraction, the first cycle, the transfer of Co from the aqueous phase to the IL is accompanied by the transfer of two Cl ions whereas from the second cycle on Co entering IL exchange with two Na ions leaving the IL. Apparently, moving in two Cl ions occurs relatively slow compared to two Na ions moving out the IL,

a different perhaps related to the fact that Cl needs to be dehydrated first before entering the IL. It is remarkable to mention that diffusivity of Cl ion in the aqueous phase is about two times faster than the diffusivity of Co ion where $D_{Cl}=2.03 \times 10^{-9} \text{ m}^2/\text{sec}$ and $D_{Co}=1.29 \times 10^{-9} \text{ m}^2/\text{sec}$. Equilibrium experiments show that the addition of n-dodecane and IPA does not influence the extraction performance of the IL significantly (Appendix 6.B.1). In addition, the equilibrium isotherms of both fresh and regenerated solvent are almost identical (taking in to account the experimental error) as shown in Appendix 6.B.2. The change in the extraction mechanism emphasizes the importance of studying the system over multiple cycles in order to get a realistic picture of the system performance.

The performance of the KARR[®] column has been evaluated using the McCabe-Thiele method. This method requires closed energy balances a condition that is fulfilled as long as the heat of mixing is negligible and the system is isothermal as well as isobaric. The operating line is a straight line and the mass balances of the solvent and the diluent are closed, a condition met if carrier and solvent are assumed to be totally immiscible [25].

Figure 6.7: Accomplished number of theoretical stages in KARR[®] column evaluated applying the McCabe-Thiele method for fresh and regenerated solvent.

Figure 6.7 illustrates the best column performance achieved using either fresh or regenerated solvent. The best performance was accomplished at an agitation rate of 250 SPM and a capacity of $20 \text{ m}^3/\text{m}^2\text{hr}$ for fresh solvent and $30 \text{ m}^3/\text{m}^2\text{hr}$ for regenerated solvent (the only capacity tested for the regenerated solvent). The number of theoretical stages achieved is 0.5 and 0.7 using fresh and regenerated solvent, respectively, corresponding to 0.8 and 1.2 theoretical stages per meter of column. This performance is relatively low compared to the results obtained for a water-acetone-toluene system [18]. This may be due to the lower interfacial tension of the water-acetone-toluene system (26 mN/m), approximately two times lower than that of the Co-water-(IL+n-dodecane+IPA) system

[18]. A lower interfacial tension allows droplet break-up more easily, resulting in small droplet formation already at low agitation intensity [26, 27]. This results in higher hold up and better mass transfer performance due to the improved interfacial area. Another important limitation is imposed by the addition of a diluent to the IL, which significantly limited the IL/Feed ratio and therefore the extraction performance.

These limitations can be overcome in different ways, namely 1) switching to a more efficient column design with an internal wall coating to allow the use of the IL without a diluent, 2) increasing the efficiency in the existing column by optimizing the selection of diluent in which lower interfacial tension can be obtained at lower IL-diluent ratios or 3) selecting a spray column with multiple droplets moving up the column.

6.4.2 KARR® COLUMN MODELLING

6.4.2.1 MODEL VALIDATION

The model was first applied to experimental data obtained from literature. Yang et al. investigated phenol extraction from an aqueous phase using the IL 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6] in a KARR® column [7]. Actually, as shown in Figure 6.8 and based on the individual mass transfer correlations (k_c and k_d), our model predicts phenol concentrations in both phases more accurately than the model used by Yang et al. based on the volumetric mass transfer coefficient (K_a). As a result, compared to the analysis of Yang, the developed model reduced AARE values of phenol concentrations from 16 % to 7 % [7].

Figure 6.8: Parity plot comparing the results of phenol concentration at outlet obtained experimentally and theoretically A) raffinate and B) extract.

Then, the model was applied to experimental data obtained for our Co-solvent system. The effect of axial dispersion is found to be negligible under the experimental conditions

applied with $Pe_a \gg 1$ (i.e., $Pe_a = 25-65$). Therefore, the plug flow model was applied for both continuous and dispersed phase with the following boundary condition at the inlet of the continuous phase instead of Eqs. (6.7) and (6.8):

$$C^c = C_{in}^c \big|_{z=H} \quad (6.12)$$

The extraction process investigated in this study differs from the system used by Yung et al., as the partition coefficient is not constant but a function of the interface concentration which complicates the numerical solution method. The continuous and dispersed phase mass transfer coefficients are predicted using the correlations developed by Kumar et al., [28]. The solute distribution, hydrodynamic prediction for the dispersed phase holdup and droplet size distribution and mass transfer coefficient for both phases enable the calculation of the column efficiency from the solution of Eqs. (6.1) and (6.2) and boundary conditions provided in Eqs. (6.9) and (6.12) using the MATLAB software.

The concentration profile of Co as function of column length, operated at a capacity of 20 m^3/m^2hr and an agitation rate of 250 SPM, is presented in Figure 6.9. It is clearly shown that the concentration changes over the aqueous phase film (difference between solid and dashed blue line) is much higher than that for the dispersed phase (difference between solid and dashed red line), indicating that the external mass transfer (i.e., aqueous phase) is dominant. For example, at the top of the column, where $m=2.3$, the external mass transfer resistance $m/k_c = 4.0 \times 10^4 \text{ sec/m}$ and the internal mass transfer resistance $1/k_d = 4.7 \times 10^3 \text{ sec/m}$. The change of Co concentration in the continuous phase is lower than that in the dispersed phase due to the low S/F ratio which is 0.58 on volume basis.

Figure 6.9: Concentration profile as function of the column height obtained using the developed model with S/F volume ratio of 0.58 at a capacity of 20 m^3/m^2hr and agitation rate of 250 SPM.

The results of the model and the experiments for the Co outlet concentration in both phases are shown in parity plots. Figure 6.10 A and B present the effect of capacity on raffinate and extract outlet Co concentration using fresh solvent and for different agitation speeds. Figure 6.10 C and D show the results per cycle for the solvent applying a fixed capacity ($30 \text{ m}^3/\text{m}^2 \text{ hr}$) and different agitation speeds 150, 200 and 250 SPM. The fresh solvent isotherm was used to run the model for the first cycle while the regenerated solvent isotherm was used to run the model from the second cycle on. In addition, the initial Co concentration in the dispersed phase varies over the cycles due to the difference in the amount of Co that remains in the solvent after regeneration. Parity plots A and B show that the results from the model based on literature correlations can predict the trends of the experimental data of fresh solvent obtained under different operating conditions including column capacity and agitation rate. The predicted results are within an AARE of 8% for the Co concentration in the raffinate and 19% for the Co concentration in the extract. However, parity plots C and D show that the model cannot predict the effect of increasing the agitation speed using regenerated solvent with an AARE of 11% for the concentration in the raffinate and 15% for the concentration in the extract. The incompetence of the model to predict the SPM trend might be related to the change in the extraction mechanism from ion pair extraction to ion exchange in the following cycles as discussed earlier. It can be deduced that the model results (based on literature correlations for mass transfer coefficients, holdup and droplet size distribution) presented in this study represents the performance of Co extraction in KARR® column with a relative error of less than 30% for most of the data points. The effect of capacity and agitation rate on the predicted mass transfer coefficient for both phases and hydrodynamic parameters including holdup and droplet size distribution are shown in Table 6.4. It is clearly shown that a high agitation speed results in a higher Co uptake despite the fact that the mass transfer resistance increases in both phases. Since the increase in mass transfer resistance is minor compared to the increase of the interfacial surface area, resulting in a higher value of k^*a .

Figure 6.10: Parity plot comparing the results of the developed model with the experimental Co concentration in both phases raffinate and extract, operating at S/F volume ratio of 0.58 and an agitation speed of either 150, 200 or 250 SPM. Panel A and B show data obtained using fresh solvent. Panel C and D show data obtained using regenerated solvent over different cycles (cycle 2-4) at column capacity of $30 \text{ m}^3/\text{m}^2 \text{ hr}$.

Table 6.4: The effect of capacity and agitation rate on the predicted mass transfer coefficient for both phases and hydrodynamic parameters including holdup and droplet size distribution obtained using correlations (discussed in Appendix 6.A). The last column presents E, a term used in the analytical solution.

Exp. No	Capacity [m ³ /m ³ hr]	SPM	u_c [m/sec] $\times 10^{-03}$	u_d [m/sec] $\times 10^{-03}$	k_c [m/sec] $\times 10^{-05}$	k_d [m/sec] $\times 10^{-04}$	d_{32} [m] $\times 10^{-03}$	Holdup [-] $\times 10^{-02}$	a [m ² /m ³]	τ_c [sec]	τ_d [sec]	E
1F-C1	20	150	3.6	2.1	8.2	2.7	8.7	2.7	18	167	286	0.12
2F-C1	30	150	5.3	3.1	7.9	2.7	8.7	4.2	29	113	194	0.13
3F-C1	38	150	6.7	3.9	7.8	2.6	8.7	5.4	37	90	154	0.13
4F-C1	20	200	3.6	2.1	7.1	2.5	6.2	3.6	35	167	286	0.15
5F-C1	30	200	5.3	3.1	6.9	2.5	6.2	5.7	56	113	194	0.15
6F-C1	38	200	6.7	3.9	6.8	2.5	6.2	7.4	72	90	154	0.15
7F-C1	20	250	3.6	2.1	5.7	2.1	4.7	5.2	67	167	286	0.14
8F-C1	30	250	5.3	3.1	5.5	2.1	4.7	8.2	105	113	194	0.14
9F-C1	38	250	6.7	3.9	5.5	2.1	4.7	10.7	136	90	154	0.14

6.5 CONCLUSIONS

KARR® column operation using the IL [P_{888}][Oleate] requires to dissolve the IL in n-dodecane and adding IPA as a demulsifier. This narrows the window of operation due to the limited IL/feed ratio and accordingly lower the extraction efficiency. The extraction efficiency of the regenerated solvent at a capacity of 30 m³/m²hr and agitation speed of 250 SPM is 48%, close to the performance of one equilibrium stage. Additionally, the extraction efficiency correlates with the agitation rate.

The experimental results obtained in this study are compared with the result of an existing counter-current plug flow model combined with literature correlations for an extraction column. The results show that the model can predict the experimental data with the right trend for column capacity and agitation rate, at least when using fresh solvent, in that case within a relative error of 30%. For reasons still unknown, the model is not able to predict similar trends when using regenerated solvent. Comparing the results of the model with the experimental data reveals AARE values < 20 for Co concentration in both continuous and dispersed phase. The generic nature of the model applied in the present study also shows from the adequate description of an IL-phenol system reported in literature and used here as testing material.

APPENDIX 6.A:

1. MODEL DERIVATION

1.1 HYDRODYNAMICS

In order to optimize the design of an extraction column, appropriate and accurate correlations are necessary to maximize the performance of the process. These correlations are used to calculate the dispersed phase drop size and holdup, mass transfer coefficients for both phases and dispersion coefficient for the continuous phase [12].

1.1.1 DROP SIZE DISTRIBUTION

a. Phenol-water-[bmim][PF₆]

To estimate the mean droplet size in reciprocating plate columns, a correlation developed by Joseph and Varma in 1998 has been used. This correlation is function of plate geometry, agitation rate and physical properties of the system which is defined as the following [29]:

$$d_{32} = 0.14 \left(\frac{\sigma}{\rho_c} \right)^{0.5} S^{0.6} (A_m f)^{-1} h_c^{0.4} d_p^{0.1} \quad (6.A.1)$$

b. Co-water-solvent

The correlation of mean droplet size developed by Rao, Srinivas and Varma in 1983 has been used for modelling the extraction of Co from aqueous phase using IL-dodecane-IPA [29]. This correlation provides a better prediction for the experimental data compared to that obtained using the correlation of Joseph and Varma Eq. (6.A.1). This is due to the higher interfacial tension of Co-water-solvent system compared to phenol-water-[bmim][PF₆]. The correlation of Rao et al., is function of agitation rate and physical properties of the system which is defined as the following [29]:

$$d_{32} = K \left(\frac{\gamma^{0.6}}{\Psi^{0.4} \rho_c^{0.2}} \right) \quad (6.A.2)$$

Where $K=0.287$ and $\Psi = 115 \rho_c (A_m f)^3$

1.1.2 DISPERSED PHASE HOLDUP

The dispersed phase holdup (i.e. volume fraction) is a fundamental factor in the design and operation of each extraction column as it is not only controlling the hydraulic performance but also it plays a crucial role in determining column diameter. In this study dispersed phase holdup has been predicted using the correlation developed by Kumar and Harland which is defined as the following:

$$\phi = [k_1 + k_2 (A_m f)^3] u_d^{0.81} (u_d + u_c)^{0.32} \Delta \rho^{-0.98} \quad (6.A.3)$$

Where, $k_1 = 3.25 \times 10^3$ and $k_2 = 7.54 \times 10^7$ in case of mass transfer direction $c \rightarrow d$ [12].

The holdup of the dispersed phase is related to the available interfacial area by the following expression:

$$a = \frac{6\phi}{d_{32}} \quad (6.A.4)$$

1.2 MASS TRANSFER COEFFICIENT

Mass transfer coefficient in extraction columns has been evaluated using the equations developed for single drops with the following extensions [28]:

- Reynolds number is evaluated with slip velocity and Sauter- mean drop diameter d_{32}
- Terminal velocity in capillary number, appearing in k_c , is replaced with slip velocity
- Effect of dispersed phase hold-up is included in k_c
- Enhancement of individual mass transfer coefficient considered with the energy dissipation per mass unit

In the continuous phase, mass transfer around drops is affected by molecular diffusion and natural and forced convection. Continue phase mass transfer coefficient depends on whether the drop is internally stagnant, circulating or oscillating [28]. The adapted correlation for calculating continue phase mass transfer coefficient in extraction columns is as the following:

$$\frac{Sh_c / (1 - \phi) - Sh_{c,rigid}}{Sh_{c,\infty} - Sh_c / (1 - \phi)} = 5.26 \times 10^{-2} Re^{\frac{1}{3} + 6.59 \times 10^{-2} Re^{\frac{1}{4}}} Sh_c^{\frac{1}{3}} \left(\frac{u_{slip} l_c}{\gamma} \right)^{\frac{1}{3}} \frac{1}{1 + \kappa^{1.1}} \left[1 + C_1 \left\{ \frac{\Psi}{g} \left(\frac{\rho_c}{g\gamma} \right)^{\frac{1}{4}} \right\}^{n_1} \right] \quad (6.A.5)$$

Sherwood number for rigid drop condition, Steiner proposed:

$$Sh_{c,rigid} = 2.43 + 0.775 Re^{1/2} Sc_c^{1/3} + 0.0103 Re Sc_c^{1/3} \quad (6.A.6)$$

To cover the data for oscillating drops, the upper limiting value of Sh_c (only for $Re \rightarrow \infty$) is defined as the following:

$$Sh_{c,\infty} = C_1 + \frac{2}{\sqrt{\pi}} (Pe_c)^{1/2} \quad (6.A.7)$$

Dispersed phase mass transfer coefficient is predicted using the following equation:

$$Sh_d = 17.7 + \frac{3.19 \times 10^{-3} \left(ReSc_d^{\frac{1}{3}} \right)^{1.7}}{1 + 1.43 \times 10^{-2} \left(ReSc_d^{\frac{1}{3}} \right)^{0.7}} \left(\frac{\rho_d}{\rho_c} \right)^{\frac{2}{3}} \frac{1}{1 + \kappa^{\frac{2}{3}}} \left[1 + C_2 \left(\frac{\psi}{g} \left(\frac{\rho_c}{gY} \right)^{\frac{1}{4}} \right)^{n_2} \right] \quad (6.A.8)$$

Where $n_1 = n_2 = 1/3$ and $C_1 = C_2 = 2.44$ for KARR® column. The term ψ represents the mechanical power dissipation for unit of mass, which is evaluated with the correlation proposed by Jealous and Johnson:

$$\psi = \frac{2\pi^2(1 - S^2)}{3h_c C_0^2 S^2} (A_m f)^3 \quad (6.A.9)$$

Where $C_0 = 0.6$ the discharge coefficient for flow through holes in the perforated plates [12, 30].

From the definition of Sherwood number Eq. (6.A.10), the mass transfer coefficient of both continuous and dispersed phase is obtained:

$$Sh = \frac{d_{32} k}{D} \quad (6.A.10)$$

1.3 AXIAL DISPERSION

The superimposition of some degree of back-mixing on plug flow is called dispersion model. Since the dispersed phase axial dispersion is negligible, the focus is given on the continuous phase axial dispersion coefficient. In this study the modified version of Prvcic correlation has been used which is defined as the following [12]:

$$E_a = \frac{K_2 (2A_m f) d_p}{S_a^{1.5}} + K_3 d_{32} \left[\frac{4g\Delta\rho u_{slip} \Phi (h_c - m_x)}{\rho_c (1 - \Phi)} \right]^{1/3} \quad (6.A.11)$$

Where;

$$m_x = K_4 \left(\frac{2A_m}{\pi} \right) \quad (6.A.12)$$

To adapt the model of Prvcic to predict the axial dispersion in KARR® reciprocating plates columns, Stella refitted the values of the parameters in Eq. (6.A.11) as the following [12]:

Table 6.A.1: Original and refitted parameters for calculation of axial dispersion coefficient

Parameters	K_2	K_3	K_4	Ref
Prvcic	0.029	0.274	1.4	[10]
Stella	0.0688	0.082	2.28	[13]

1.4 ANALYTICAL SOLUTION

The plug flow model is the simplest model in which it is assumed that in each phase all elements have the same residence time in the KARR® column. In the studied system, the continuous phase flows from top to bottom and the dispersed phase flows from bottom to top as shown in Figure 6.1. The length (H) axis has its positive direction from bottom to top. Hence the continuous phase velocity is negative in this coordinate system. Taking the absolute values of the velocities in both phases, the governing differential equations for the continuous and dispersed phase are set up by writing mass balances for the two phases over a differential control volume under steady state conditions.

For the continuous phase:

$$\frac{dC_c}{d\theta} = K * a * \tau_c * (m * C_c - C_d) \quad (6.A.13)$$

For the dispersed phase:

$$\frac{dC_d}{d\theta} = K * a * \tau_d * (m * C_c - C_d) \quad (6.A.14)$$

Where;

$$\theta = \frac{z}{H} \quad (6.A.15)$$

$$\tau = \frac{H}{u} \quad (6.A.16)$$

$$m = \left(\frac{C_d}{C_c} \right)_{int} \quad (6.A.17)$$

$$K = \frac{1}{\frac{m}{k_c} + \frac{1}{k_d}} \quad (6.A.18)$$

These differential equations are solved using the following boundary conditions:

For the continuous:

$$\text{At } \theta = 1 \rightarrow C^c = C_{in}^c \quad (6.A.19)$$

For the dispersed phase:

$$\text{At } \theta = 0 \rightarrow C^d = C_{in}^d \quad (6.A.20)$$

This system of equations can be solved analytically by using linear differential operator method, the results are as follows:

$$C_c(\theta) = \frac{(C_{c,in} * \tau_d - C_{d,in} * \tau_c * e^E) + \tau_c * e^{\theta E} (C_{d,in} - C_{c,in} * m)}{Z} \quad (6.A.21)$$

$$C_d(\theta) = \frac{m * (C_{c,in} * \tau_d - C_{c,in} * \tau_c * e^E) + \tau_d * e^{\theta E} (C_{d,in} - C_{c,in} * m)}{Z} \quad (6.A.22)$$

Where;

$$E = K * a * (m * \tau_c - \tau_d) \quad (6.A.23)$$

$$Z = \tau_d - m * \tau_c * e^E \quad (6.A.24)$$

Figure 6.A.1 shows that the concentration profile for both phases obtained using the analytical solution are in full agreement with the results of the numerical solution obtained using the MATLAB model.

Figure 6.A.1: Concentration profile obtained for analytical and developed MATLAB model. The applied tolerance is $0.1[\text{mol}/\text{m}^3]$ which is defined as the difference between concentration predicted by the model and the measured concentration.

Table 6.A.2 and 6.A.3 tabulated the system properties, column characteristics and model parameters used in the analytical solution respectively.

Table 6.A.2: System properties and column characteristics used in Co-Water-solvent experiments.

properties	Value	Unit
System properties		
Continuous phase	Water-Co	[-]
Dispersed phase	$[\text{P}_{888}][\text{oletate}]\text{-n-dodecane}$	[-]
ρ_c	1030	$[\text{kg}/\text{m}^3]$
ρ_d	$793 \text{ kg}/\text{m}^3$	$[\text{kg}/\text{m}^3]$
μ_c	0.001	$[\text{Pa sec}]$
μ_d	0.014	$[\text{Pa sec}]$
Interfacial tension	0.045	$[\text{N}/\text{m}]$
Column characteristics		
Diameter	15.9	$[\text{mm}]$
Column effective height	60.1	$[\text{cm}]$
Number of plates	24	[-]
Plate spacing	25.4	$[\text{mm}]$
Perforation diameter	6.32	$[\text{mm}]$
Plate free area	55	$[\%]$

Table 6.A.3: Parameters used to validate MATLAB model with analytical solution.

Parameters	Value	Unit
u_c	0.0067	[m/sec]
u_d	0.0039	[m/sec]
a	237	[m ² /m ³]
m	1.3	[-]
C_{in}^c	84.89	[mol/m ³]
C_{in}^d	0	[mol/m ³]
k_c	6.10×10^{-5}	[m/sec]
k_d	2.04×10^{-4}	[m/sec]

1.5 IMPLEMENTATION IN MATLAB

The solution of the coupled governing equations with referred boundary conditions will lead to the profiles of Co concentration in the continuous and dispersed phase as a function of column length. As observed in Eqs. (1) and (2), in order to determine the concentration of Co in the continuous phase, the concentration of Co in dispersed phase and at the interface is required. At the interface, the equilibrium concentration between the continuous and dispersed phase is defined by an algebraic function as discussed in 2.1. The governing equations are solved in a simultaneous manner using MATLAB's initial value problem (Ivp) solver ode15s since the built-in boundary value problem solver (bvp4c) is incapable of handling algebraic equations. Thus, the shooting method has been implemented to incorporate the boundary conditions required to solve the governing equations.

APPENDIX 6.B

Batch extraction was performed using feed solutions containing 0.1-60 g/L Co and Na from their corresponding Cl salts at room temperature. In each experiment, 5 ml aqueous phase mixed with 5 ml of fresh or regenerated water-saturated $[P_{888}][Oleate]$ for 10 min at 40 rpm and centrifuged (3750 rpm; 10 min, 22°C). NaCl was used as a salting-out reagent to improve the extraction efficiency.

Figure 6.B.1: Fitted equilibrium curves obtained from the experimental data of fresh and regenerated solvent (IL+n-dodecane with addition of IPA). Note, Co concentration in all cases is relative to the amount of solvent applied. Dashed square represents the region where KARR® column experiments were performed.

Figure 6.B.2: Equilibrium curve for pure IL, fresh and regenerated solvent (solvent means IL+n-dodecane with addition of IPA). The Co concentration on the Y-axis is relative to the amount of IL present. Note, the amount of extracted metal is small and hardly change the volume of the IL.

APPENDIX 6.C:

Table 6.C.1: Co extraction obtained using fresh solvent (1st cycle) at different capacity and agitation rate.

Exp. No	Capacity [m ³ /m ² hr]	Throughput [ml/min]	Feed Flow [mL/min]	Solvent Flow [mL/min]	SPM	[Co] _{Raff} [g/L]	[Co] _{Extract} [g/L]
01F-C1	20	67	42.3	24.7	150	3.86	1.95
02F-C1	30	100	42.3	24.7	150	3.95	1.80
03F-C1	38	126	42.3	24.7	150	4.03	1.67
04F-C1	20	67	63.1	36.9	200	3.71	2.21
05F-C1	30	100	63.1	36.9	200	3.74	2.15
06F-C1	38	126	63.1	36.9	200	3.65	2.31
07F-C1	20	67	79.5	46.5	250	3.25	2.99
08F-C1	30	100	79.5	46.5	250	3.31	2.89
09F-C1	38	126	79.5	46.5	250	3.35	2.82

Table 6.C.2: Co extraction obtained using regenerated solvent (2nd – 4th cycle) at a capacity of 30 m³/m²hr and agitation rate 150, 200 and 250 SPM

Exp. No	SPM	[Co] _{Raff} [g/L]	[Co] _{Extract} [g/L]
01R-C2	150	3.22	3.05
02R-C2	200	3.09	3.27
03R-C2	250	2.83	3.72
04R-C3	150	3.23	3.04
05R-C3	200	3.14	3.18
06R-C3	250	2.70	3.93
08R-C4	150	3.00	3.43
09R-C4	200	2.89	3.61
10R-C4	250	2.63	4.06

Nomenclature

Symbols	Description	Unit
a	Specific interfacial area $\left(\frac{6\phi}{d_{32}}\right)$	m^2/m^3
A	Interfacial area	m^2
A_m	Amplitude	m
C	Solute concentration	mol/m^3
D	Diffusion coefficient	m^2/sec
d_{32}	Sauter mean drop diameter	m
d_p	Plate perforation diameter	m
E_a	Axial dispersion coefficient	m^2/sec
f	Frequency	$1/\text{sec}$
H	Effective height of the column	m
h_c	Plates spacing	m
K	Overall mass transfer coefficient	m/sec
k	Partial mass transfer coefficient	m/sec
m	Partition coefficient	-
m_x	Height of fully mixed region	m
M_i	Molecular weight of component i	g/mol
N	Number of experiments	-
NTS	Number of theoretical stages	-
Pe_a	Peclet number $\left(\frac{Hu_c}{E_a}\right)$	-
Pe	Peclet number $\left(\frac{d_{32}u}{D}\right)$	-
Q	Volumetric flow rate	m^3/hr
R	Ratio of continuous to dispersed phase velocity $\left(\frac{u_c}{u_d}\right)$	-
Re	Reynolds number $\left(\frac{\rho u d_{32}}{\mu}\right)$	-
S	Fractional open area of plates	-
S_a	Cross sectional area of column	m^2

Sc	Schmidt number $\left(\frac{\mu}{\rho D}\right)$	-
Sh	Sherwood number $\left(\frac{k_d d_{32}}{D}\right)$	-
S/F	Solvent to feed ratio	-
u	Superficial velocity	m/sec
u_{slip}	Slip velocity	m/sec
V	Droplet volume	m ³
wt.	weight fraction	%

Greek letters

γ	Interfacial tension	N/m
κ	Viscosity ratio $\left(\frac{\mu_d}{\mu_c}\right)$	-
φ	Holdup	-
ρ	Density	kg/m ³
σ	Surface tension	N/m
ψ	Mechanical power dissipation per unit mass	W/kg
μ	Viscosity	Pa sec
η	Extraction efficiency	%
τ	Contact time	sec

Superscripts

c	Continuous phase
d	Dispersed phase

Subscripts

c	Continuous phase
d	Dispersed phase
E	Extract
in	Inlet
int	Interface
R	Raffinate

Abbreviations

BTU	Bench top unit
Bvp	Boundary value problem
equ	Equilibrium
lvp	Initial value problem
IL	Ionic liquid
IPA	2-propanol
KMPS	Koch modular process systems
AARE	Average absolute relative error
PTFE	Polytetrafluoroethylene
SPM	Strokes per minute

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CHAPTER 7

CONCLUSIONS AND OUTLOOK

There is never an end just a new beginning

Joseph P. Sekula

7.1 CONCLUSIONS

The aim of this PhD thesis was to address several aspects of upscaling a liquid-liquid extraction (LLX) process that uses an already existing ionic liquid (IL) rather than the development of an entirely new IL. This PhD thesis combines the results of five different research lines, each involving the use of the fatty-acid-based ionic liquid $[P_{888}][\text{Oleate}]$ for the extraction and separation of critical metal ions. Each chapter in this series of studies aims to reflect on one of the main stages in designing and developing the LLX process and include (1) carrying out batch scale fundamental analysis, (2) exploring industrial application(s) (3) understanding the underlying extraction mechanism, thermodynamic behaviour and physicochemical properties of the process and process streams (4) performing experimentally and numerically-based mass transfer and reaction kinetic investigations, and (5) operating the process on a lab scale extraction column.

Based on the available literature, IL $[P_{888}][\text{Oleate}]$ is a promising candidate for metal extraction, which is mainly due to its ability to selectively extract transition metals. Furthermore, the selectivity can be adjusted depending on the pH and composition of the aqueous solution. Moreover, it is claimed that the losses of this IL to the environment are limited compared to a (classic) volatile organic solvent due to its negligible vapour pressure. In **Chapter 2**, as a proof-of principle, $[P_{888}][\text{Oleate}]$ has been utilized to extract Co from an artificial chloride-based industrial process stream. The loaded IL was then regenerated using different concentrations of Na_2CO_3 , with the goal of producing CoCO_3 as a marketable end product. This process was operated for five cycles and it was possible to extract and recover up to 99% of the initially present Co in the feed solution. The main outcome of this chapter is that the transfer of Co shifted from ion-pair extraction in the first cycle to ion-exchange in the successive cycles. This finding indicates that the measurement of a single extraction–regeneration cycle is not sufficient to obtain conclusive information about the steady-state conditions of the process with respect to efficiencies, recoveries, and the mechanism of the ion transfer mechanism. Furthermore, this chapter defines the extraction efficiency, recovery of the IL and of the metal, loss of the IL, and the nature of the end product as the key parameters that determine the potential feasibility of any LLX process using ILs.

Chapter 3 explores a new separation method to selectively recover Co, Ni, Mn and Li from synthetic HCl-based leachates of spent Lithium Ion Battery (LIB) cathodes. The investigated parameters for this selective separation and recovery process included the extraction pH, contact time and composition of the regeneration solution. The benefit of using this IL is that >99% of Co and >99% of the Mn can be separated from the Ni and Li by a two-stage extraction process. The subsequent separation of Mn from Co is achieved by a regeneration process using a composite solution containing ammonia, ammonium

carbonate and ammonium sulphate, where Co remains in the raffinate and Mn precipitates as MnCO_3 . Ni and Li are successfully separated using Na_2CO_3 as regeneration solution, due to the difference in the solubility product of the two carbonate salts. The regenerated IL is then directly re-used in the subsequent extraction cycles. The three key parameters that determine the potential economic feasibility of the process outlined here are the Co concentration in the leachate solution, the molarity of the HCl used and the market price of Co. An EP0 analysis including these parameters revealed that in terms of economics the use of 4 M HCl is preferred despite the fact that 8 M HCl showed the highest extraction efficiency for both Co and Mn. Using a 4 M HCl leachate solution, the break-even point, i.e. $\text{EP0} = 0$ (based on a cobalt price of 35 \$/kg) was reached by using leachates containing at least 4.5 g Co per liter. While using 4 M HCl leachates with lower Co concentration (3 g Co per liter), EP0 can be achieved once the Co price exceeds 48 \$ per kg (see Figure 3.7).

Chapter 4 addressed several issues related to the thermodynamic behaviour of metal extraction using IL $[\text{P}_{888}][\text{Oleate}]$ such as metal affinity, extraction mechanism, in addition to sensitivity toward the composition of the aqueous solution. It is known that metal ions exist in aqueous phases as hydrated species and, as such, are incompatible with the applied IL [1, 2]. Therefore, to achieve extraction, these metal species must be modified to make them more hydrophobic by following a series of elementary steps: (1) reaction of the metal cation with suitable anions to produce a neutral metal salt, (2) extraction of the metal salt into the organic phase, and (3) replacement of hydration water molecules by an organic reagent [1, 2]. Three different models were evaluated, all different with respect to the Co species that complexes with the IL. This analysis points towards the presence of CoCl_2 within the IL as a metal-IL complex. Additionally, it revealed that the extraction of Co has a positive enthalpy and entropy value, which indicates an endothermic, spontaneous entropy-driven complexation LLX process. The occurrence of an endothermic complexation reaction between the IL and the extracted Co salt was supported by Co activity calculations and conductivity measurements. The higher the temperature, the lower the activity coefficient ratio $\gamma_{\text{CoIL}}/\gamma_{\text{Coaq}}$ and the lower the free Co activity in the IL itself. Besides, the higher the concentration of Co in the IL, the lower the measured electric conductivity. The extraction behaviour of the IL was also affected by (1) the ability of the extracted metal salt to complex with the IL, (2) the nature of the accompanying anion, and (3) the presence of a salting-out agent. The higher propensity of Co for complexation with the IL compared to Na, resulting in a higher extraction of Co. The difference between the affinity of the IL for Co and Na is evident from the difference in shape of both isotherms. Whereas the extraction of Co follows a Freundlich-type of isotherm, the extraction isotherm of Na is essentially linear. The higher Co extraction from a NO_3 medium is due to the stronger interaction between $\text{Co}(\text{NO}_3)_2$ and the IL, reflected by a higher equilibrium constant of $\text{Co}(\text{NO}_3)_2$ (i.e., $K_{\text{eq}} = 3.3 \times 10^{+2}$) versus the one for CoCl_2 (i.e., $K_{\text{eq}} = 1.5 \times 10^{+1}$), both fitted for a complexation reaction with a Co:IL ratio of 1:2, performed

at room temperature. Finally, the observed difference in Co uptake in the presence of salting-out agent (NaCl, KCl and NH_4Cl) can be explained in terms of the hydration energy of the salting out cation. The higher this energy (i.e., the more negative), the less water available for the hydration of Co and the less dehydration required for its uptake, all resulting in a higher Co uptake.

In **Chapter 5** the main focus was investigating the mass transfer behaviour and reaction kinetics of Co extraction from an aqueous solution by single $[\text{P}_{888}][\text{Oleate}]$ IL droplets. A statistical cross-validation method was used to evaluate different mass transfer models, with and without the presence of a chemical reaction. It was concluded that a mass transfer model with just a single fitting parameter, Sherwood number of the continuous phase, adequately describes the extraction of Co for the whole data set with most of the experimental data predicted within $\pm 30\%$, regardless of the initial solute concentration in the continuous and dispersed phase, contact times or droplet diameters. Adding a chemical reaction to the model does not improve the predictions significantly. At first sight, this finding seems to contradict the conclusion of **Chapter 4**, presenting clear evidence for an interaction between Co and the IL. However, if taking into account the very short contact time during the single droplet extraction experiments and the slow complexation reaction between the extracted Co salt and the IL, the conclusions of both chapters line up. Unfortunately, due to the change of the physical properties (mainly viscosity) of the loaded IL, the parameters determined from extraction experiments were not able to describe the back extraction of Co. The increment in viscosity of the loaded IL reduces the diffusivity of Co within the IL and hinders the internal circulation observed during extraction experiments. Therefore, a mass transfer model for the back extraction of Co was evaluated using literature correlations applicable to rigid, stagnant spheres.

A first step towards scaling-up the Co extraction process is reported in **Chapter 6**. Applying $[\text{P}_{888}][\text{Oleate}]$ for extraction of Co in a continuous mode mixer-settler resulted soon after the start in the formation of a stable emulsion, limiting the applicability of the process after only a limited number of cycles. A KARR® reciprocating plate column with 5/8" diameter was selected and used for its ability to handle mixtures with emulsifying tendencies. Unfortunately, $[\text{P}_{888}][\text{Oleate}]$ shows a strong propensity to adhere to the glass and metal surfaces of the column upon, already right after the onset of Co extraction. Therefore, it was necessary to dissolve the IL in n-dodecane to be able to create solvent droplets with a much lower tendency to surface adherence. To avoid emulsification using the regenerated solvent, isopropyl alcohol was added as a demulsifying agent. This narrowed the window of operation due to the limited IL/feed ratio and accordingly lowered the extraction efficiency. Increasing the column capacity from 20 to 38 $\text{m}^3/\text{m}^2\text{hr}$ had no significant effect on the extraction efficiency. This was ascribed to a balance between the positive effect of increased interfacial area resulting from a higher hold up which is function of the

continuous and dispersed phase velocity, and the negative effect of reduced contact time. Increasing the agitation rate from 150 to 250 SPM improved the extraction performance from 36% to 48%, which is close to the performance of one equilibrium stage per meter of column. This improvement in the extraction efficiency is attributed to the increase of interfacial area available for mass transfer resulting from a smaller droplet size and higher holdup. A mathematical model, including literature correlations for mass transfer, holdup and droplet diameter, was also developed. The model results were compared with experimental data obtained in this study as well as with one study found in the literature. The model was able to predict experimentally observed trends (e.g. efficiency as a function of capacity) and the absolute extraction performance with an AARE of less than 20%.

7.2 OUTLOOK

Recovery of valuable metals from different process streams including synthetic wastewater streams from mining industries or spent lithium ion battery leachate was studied in this dissertation. The content of this thesis can be regarded as a first step towards upscaling a potential LLX process using an IL. From an economic point of view, this process would be feasible for a concentrated cobalt-containing wastewater stream or spent lithium ion battery leachate. Otherwise, an efficient full-scale industrial process might require a pre-concentration step of the aqueous solution before the extraction step with IL in order for the process to be economically viable. Potential pre-concentration technologies include reverse osmosis and forward osmosis, both with their own specific advantages and disadvantages (e.g., regarding the optimal range of feed Co concentration) [3].

Working towards upscaling this LLX process, some important issues were encountered that are not yet completely answered. The most important issue identified is the necessity of adding a diluent and a demulsifying agent to operate the LLX process in a KARR® reciprocating plate extraction column. Two other issues encountered during the study were the slow mass transfer rate of back extraction and the lack of clear evidence behind the environmental profile of the applied IL, and especially so in the setting where it is used for the purpose of wastewater treatment as intended in this study.

7.2.1 UPSCALING LLX PROCESS

One of the challenges that will be interesting to investigate further is finding alternatives that will allow eliminating the need for adding diluents and de-emulsifying agents in the KARR® reciprocating plate extraction column. Although these agents have a positive impact in terms of controlling flooding inside the columns, they narrow the operational window as they heavily limit the IL-to-feed ratio and, with that, the extraction performance as well. To avoid the addition of these agents, three different options could be explored.

First, switching to a more efficient column design with an internal wall coating that allows the use of the IL without a diluent. For example, coating the internal glass wall and stainless-steel reciprocating plate stack of the extraction column with a non-ionic polymer can most probably remedy this problem. However, the particular polymer (for instance polystyrene or polypropylene) should withstand the rather harsh experimental conditions. Batch experiments performed using vials made of these types of polymers show no electrostatic interaction with the loaded IL. Secondly, increasing the efficiency in the existing column by the selection of a diluent in which a lower interfacial tension can already be obtained at lower diluent-IL ratios. In literature, the use of an IL as a diluent shows a potential toward improving the physical properties of the extractants (ILs). For example, the IL choline bis(trifluoromethylsulfonyl)-imide, [Chol][Tf₂N], was successfully used as a diluent for the IL choline hexafluoroacetylacetonate, [Chol][hfac], and applied in the extraction of the lanthanides [4]. Thirdly, selecting another type of contactor, for instance, a spray column with multiple droplets simultaneously moving up the column. Experiments performed using a single droplet extraction column (see **Chapter 5**) already showed that it is indeed possible to use the IL without any diluent or de-emulsifier. When using a spray column, it is crucial to select the correct operational conditions, for instance, regarding the prevention of coalescence, eventually leading to phase separation. In conclusion, investigating different columns, including wall coatings, and different diluents and de-emulsifiers is needed to further optimize the process of IL-based LLX in a column.

7.2.2 RATE OF BACK EXTRACTION

The second challenge that the carried investigations identified was the slow rate of mass transfer during the back-extraction process compared to that during forward extraction. As described in **Chapter 5**, the complexation of IL with the extracted Co dramatically increased the viscosity of the organic medium and contributed to slowing down the rate of back-extraction. One solution to this problem that was explored is the use of an electrical force for the purpose of increasing the rate of mass transfer. A technique that uses electric field-enhanced mass transport is electrohydrodynamic atomization (EHDA) or electrospray [5-7]. EHDA is a physical process caused by the electric force applied to the surface of the liquid [8]. The electrical stress elongates the liquid meniscus formed at the outlet of the nozzle, forming into a cone and/or a jet which then disintegrates into small droplets because of the electrical force [8]. In EHDA the electric field is created by establishing an electric potential difference between the nozzle and a counter electrode placed at a certain distance from the nozzle's tip. For a certain nozzle-counter electrode configuration and a specified liquid, different spraying modes can be obtained depending on the applied potential difference, and the liquid flow rate. The most known nozzle-counter electrode configuration are nozzle-plate, nozzle-ring and coaxial cylindrical nozzle [5]. In order to create encapsulated droplets and to enhance the mass transfer rate during IL regeneration, A coaxial cylindrical nozzle configuration can be applied.

This configuration allows the enlargement of the interfacial area between the two phases and accordingly increasing mass transfer rate as a result of droplet encapsulation and elongation as well as the formation of a smaller droplets. Although this technology was briefly investigated - and showed promising results - this concept was not fully explored in this study due limited resources. It is certainly worthwhile to further explore this solution and assess its impact on the back-exchange step of the process.

7.2.3 TOXICITY

A large push for the shift in industry towards the use of ILs is the anticipated relatively lower environmental impact. However, it remains to be investigated how the use of IL in the described LLX process interacts with the environment throughout its entire life-cycle. Although the three main pillars of sustainability (i.e., economic, environmental and social) and reusability of the IL have been expounded on in this study, the environmental impact associated with their synthesis, use as well as disposal are equally important factors that cannot be overlooked. The loss of IL to the environment is still a matter of debate. For example, constraining the IL 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim] [PF_6] in membrane pores showed, over 250 hrs, losses of around 1.5×10^{-2} M to the aqueous phase [9, 10]. Although this concentration is lower than the solubility of this IL in water, 6.76×10^{-2} M, the loss is not negligible [9]. Sceptics of the green profile of ILs indeed argue that the advantage of ILs regarding their negligible volatility is counteracted by their losses to the aqueous phase. In **Chapter 2**, it is reported that the loss of [P_{888}][Oleate] to the aqueous phase is less than 15 ppm, i.e., the loss of IL per cycle is $< 0.002\%$ [11]. Even though this may seem quite small, it deserves serious attention. If not, the IL phase will gradually disappear out of the system, rendering a process that is both unsustainable and economically non-feasible.

7.2.4 ILs IMPLEMENTED IN MEMBRANE TECHNOLOGY

Given the current trend of the electrification of industrial processes, one option to discuss is the implementation of ILs in an electrodialysis (ED) setting with the ILs immobilized in the central membrane. The IL may be present either in some type of a supported liquid membrane (SLM) (possibly sandwiched between two membranes in order to prevent leakage, as discussed in the previous section) or in some kind of a polymer inclusion membrane (PIM) [12, 13]. Under ED operational conditions, be that in the constant voltage or the constant current mode, ion migration and with that mass transport is enhanced by the externally applied electric field. In that sense, ED may also be the solution to the observed slow back extraction referred to in the previous section. One of the key aspects to investigate is whether or not under the condition of forced ionic current the IL-based membrane retains its Co selectivity. In order to make the IL-based membrane technology meet the criteria defined in **Chapter 2**, the concentrate solution should contain an anion species that precipitates with Co, e.g. carbonate, producing an end product of clear economic potential.

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If I have seen further it is by standing on the shoulders of Giants

Isaac Newton

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Enas Othman

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ABOUT THE AUTHOR

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Enas Azhar Othman was born on the 2nd of June 1988 in Nineveh, Iraq. She moved to Qatar in 1999 where she grew up and spent most of her life. In 2012 she obtained her Bachelor of Science degree in Chemical Engineering and graduated with highest GPA among her graduating batch. The title of her bachelor's thesis was Carbon dioxide (CO₂) capture and conversion from natural and effluent gas streams. She completed this project under the guidance of dr. Mert Atilhan. In 2014, she was awarded her Master of Science degree in chemical engineering at Texas A&M University and graduated with honours. The title of her master's thesis was Gas Hydrate Equilibrium Measurements for Multi-component Gas Mixtures and the Effect of Ionic Liquid Inhibitors. This project was conducted under the supervision of both Prof. Marcelo Castier and dr. Mert Atilhan. In the summer of 2014, she moved to the Netherlands and in 2016 she started her PhD in chemical engineering at the University of Twente in the Sustainable Process Technology (SPT) group under the supervision of Prof. Sascha Kersten. The aim of her project is the development of liquid-liquid extraction process to selectively recover valuable metals from different industrial process and waste streams. The research was carried out at Wetsus, European Centre of Excellence for Sustainable Water Technology.

SCIENTIFIC OUTPUT

SCIENTIFIC OUTPUT

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