THE SELECTIVE SEPARATION AND EXTRACTION OF METALS USING MEMBRANE TECHNOLOGY

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DECLARATION

“I Alexandra Blitz-Raith declare that the Masters by Research thesis entitled “ The Selective Separation and Extraction of Metals Using Membrane Technology “ is no more than 60,000 words in length exclusive of tables, figures, appendices, references and footnotes. This thesis contains no material that has been admitted previously, in whole or on part, for the award of any other academic degree or diploma, except where otherwise indicated, this thesis is my own work.”

Signature Dated 21st November 2012

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PUBLICATIONS

1. Blitz-Raith, A. H., Paimin, R.;Kolev, S. D. (2005). The application of polymer liquid membranes to the extraction of cobalt(II) from aqueous solutions. International Solvent Extraction Conference, China.

2. Blitz-Raith, A. H., Paimina, Rohani , Cattrall, Robert W. and Kolev, Spas D. (2007). "Separation of cobalt(II) from nickel(II) by solid-phase extraction into Aliquat 336 chloride immobilized in poly(vinyl chloride)." Talanta **71**(1): 419-423.

3. Provisional Patent No 2007900692 titled “Separation of Cobalt, Nickel and Iron in aqueous Solutions"

Abstract

The separation of Co(II), Ni(II) , Fe(II) and Fe(III) has been a problem that has vexed chemists for many years. Separation has been difficult because of the very similar chemical properties of these transition metals that are situated alongside each other in the Periodic Table.

The work contained in this thesis shows the membrane extraction of the metals: Cobalt(II), Nickel(II). Iron(II) and Iron(III) in aqueous media using a polymer “entangled” membrane containing the extractant Aliquat 336 and PVC (polyvinylchloride).

The studies of each metal were carried out in a variety of aqueous chloride, sulphate and nitrate media and it was found that the efficiency of the extraction was dependent upon the concentration of the anion in solution. The stripping of the metal was completed using deionised water for each of the metals and the back extraction studies were then used to identify the metal complexes that were formed in the matrix of the membrane and hence to postulate the mechanism of the extraction in each case.

The ultimate aim of the thesis was to show the selective separation and extraction of Cobalt(II) from Nickel(II) and Nickel(II) from Cobalt(II) in aqueous chloride, sulphate and nitrate media and then the selective separation of these metals from Iron(II) and Iron(III) in the same media. This was achieved using the information from the individual extraction studies of each metal that were carried out in the aqueous media.

The innovative work in this thesis presents for the first time the selective separation of the three transition metals in a variety of aqueous media using a membrane that contained Aliquat 336/PVC. The process has a Provisional Patent Number 2007900692, titled “Separation of Cobalt, Nickel and Iron in aqueous solutions”.

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Chapter One

1.1 Introduction

Cobalt and nickel are transition metals of significant industrial and economic importance. In the Earth's crust they are estimated to have an abundance of 0.003% and 0.0089% respectively, of which 60% is in accessible mineral deposits, predominantly laterite, where they occur as cobalt and nickel oxides in combination with iron oxides and must be extracted from the surrounding matrix and then separated [1].

The wastewater resulting from the separation processes also needs to be cleaned and the trace metals removed. There are difficulties in cleaning the metals and organic solvents from the wastewater that need to be addressed, because of their toxicity and potential to cause pollution and contamination in both water and soil.

These transition metals, Fe, Co and Ni which have atomic numbers 26, 27 and 28 respectively, share similar densities, high melting points and high boiling points. In addition, all have partially filled "*d*" orbitals which accounts for the remarkable similarity in their physical and chemical properties. Together, these similarities make extraction and separation of the three metals and their metal ions somewhat difficult.

The next sections briefly consider the traditional methods of metal extraction from ore deposits, and the current technologies that are used to achieve this. Also considered are the reasons for the need of the removal and extraction of the trace metals from wastewater.

1.2 Traditional metal extraction from ore deposits

The production of nickel from laterite ores has occurred for over 100 years [2].
Historically the main source for primary nickel product has been the nickel-iron-copper sulphide ores containing 1-3% nickel that are found deep underground and mining for these metals becomes very expensive [3]. The sulphide ores represent about 30% of the world's nickel

resources. The remaining 70% are represented by the nickel-ferrous lateritic ores, which are also a major source of cobalt and are located closer to the earth's surface [3].

The traditional extraction methods to remove these metals from the gangue material have included pressure acid leaching of the solid phase laterites using horizontal agitated autoclaves, and although the design of these autoclaves has improved in recent years better methods of separation have been found [3]. The main improvement in separation has been solvent extraction, which has been influenced by the development and commercial availability of new solvent extraction reagents and improvements in the design and engineering of solvent extraction equipment [3].

Sulphide or hydroxide precipitation before solvent extraction has also been a method used for recovery of nickel and cobalt [2, 3, 4], but with the increased worldwide pressure to find and operate in a more environmentally friendly manner more research has been necessary to improve the technologies by which extraction processes are carried out.

1.3 Extraction and separation from aqueous solution

Direct solvent extraction for metals has been used for the past 60 years with the first application being the recovery of uranium. Some 10 years later, solvent extraction of copper was introduced [4]. Following this successful work with copper, there have been many solvent extraction plants that have been used for the recovery of other metals including cobalt and nickel, most of these being mixer settler in design [4]. Sulphate is the most common media that has been used along with some chloride-based systems. These methods were seen as having great potential provided that a highly selective, stable and inexpensive extractant could be found [5].

More recently, direct solvent extraction processes with the use of a variety of membranes and extractants and organic solvents have been used to advantage. The most common commercial extractants that have been used include cation, chelating, anion and solvating chemicals [5] and whilst these extraction methods have been used with some success, there are a number of factors that make these approaches unsatisfactory. These include the degradation of some extractants at high temperatures, poor phase separation and solvent

degradation and solvent losses [6]. Other factors that have a direct influence are the economy, cost factors and more importantly environmental concerns. Some examples of the chemicals used in the leaching process include hydrogen sulphide, ammonia and concentrated sulphuric acid as well as organic extractants such as Cyanex 272 and D2EHPA, Lix 841 which are used in the metal stripping process. The reoximation (restoration of the extractant in the organic phase), can cause organic degradation [3]. Aromatic diluents that are used to remove the amine organic extractants and the use of aliphatic diluents have a lower flash point, but are more volatile and are a fire hazard [3]. In these processes the required chemicals and solvents, some of which are highly volatile, are not only expensive and come predominantly from the petrochemical industry, but are also difficult to dispose of in an environmentally friendly and appropriate manner.

These disadvanages mean that the identification and development of alternative extraction methods will be essential in the future and in this respect the use of membrane technolgy that does not use organic solvent would be very advantageous. Also it would be important to develop a system that could be used in situations where there are high concentrations (such as metal extraction from ore) and low concentrations (in waste and clean-up processes) of these valuable metal ions

1.4 Trace metal extraction from wastewater

There are a number of industrial circumstances, such as those detailed below, where cobalt, nickel and iron are present in wastewater, which requires cleaning before discharge into the environment. In addition, in many cases the waste stream represents a recoverable source of cobalt and nickel, which are relatively valuable metals. Again this suggests that the search for an economically viable extraction system, which is capable of separating these metals in the presence of a variety of anion species and across a wide range of pH will be required.

The extraction of cobalt and nickel has led to many environmental concerns, in particular the pollution of groundwater. This pollution has occurred as a result of the acidic drainage from mines and mining processes and from the wastewaters that may contain toxic metals including arsenic, cobalt and nickel. Cyanide that is commonly used in extraction and separation processes is also found in the wastewaters from chemical refining practices and there are often suspended solids and sludge in the residuals that may affect plant and marine life. This was reported by Gikas [7] in a recent journal article on the ‘single and combined effects of cobalt and nickel ions in activated sludge’. These studies were particularly useful in establishing criteria for the heavy metal tolerance levels in the environment and for establishing the fact that conventional wastewater treatments may only partially remove these metals and metal complexes from the waste.

Further, solvent extraction processes in the ore refinement [8], metal finishing [9] and electroplating [10, 11, 12] industries give rise to waste streams that require treatment before discharge, and in each of these cases, there are significant concentrations of associated anions such as nitrate, sulphate and chloride and other metals which can cause traditional extraction methods to fail. The high concentration of chloride solution is very corrosive and difficult to handle, as is the sulphate and nitrate that is used in acid leaching processes of the ore [2].

A final consideration, which is a relatively recent development, is that the water used in many extraction procedures will be required for recycling, demanding that the metallic residues and anions be removed from large volumes of wastewater efficiently and cheaply.

1.5 The role of enabling technologies

One of the most encouraging directions in metal separation advances is membrane technology, and it is with these methods that this investigation will be concerned. The role of these physical separation processes can be described as “enabling technologies” and are discussed in detail in a paper by Sikdar *et al*. [13]. These authors also outline some common environmental problems and suggest opportunities for the introduction of innovative separation technologies which include the application of membrane technology [13].

Membranes have existed in various forms in both biology and botany for centuries and they have been recognized and widely discussed for their transport properties of both gases and liquids [14]. The use of membrane separation processes can offer advantages such as high selectivity, low energy consumption, moderate cost to performance ratio and compact design in modern separation technology, These advantages and some disadvantages are reviewed in a paper by Suk *et al.* [15], which will be discussed further in Chapter 2.

Currently membrane technology has become one of the fastest growing areas of modern chemistry because of their importance in solvent extraction processes. These processes form the basis of metal separation techniques particularly in hydrometallurgy [16, 17]. They have been used to separate cobalt and nickel from sulphate leach solution during ore refinement, for the removal of metals such as nickel and zinc and chromium that are commonly found in electroplating wastewaters [10, 11, 12], hazardous waste reduction such as the removal of metals including nickel and zinc, metal finishing wastewaters [9], and the general treatment of wastewater from a range of industrial sources [18, 19, 20, 21].

1.6 The focus of this investigation

The extraction and separation of trace amounts of cobalt and nickel has been a problem that has perplexed chemists for decades. Because of their chemical and physical similarities, a key part of the problem is the inability to achieve a satisfactory degree of separation even when a large number of separation stages are used [4, 5]. In addition, as has been mentioned, the current solvent extraction techniques are becoming problematic because of the ancillary chemicals employed, an issue clearly identified by Ritcey [5, 6]. Whilst these papers also consider the past and possible future applications of solvent extraction, they also mention membrane technology, introducing the notion that the development of liquid and supported membrane technology is of scientific importance to the future of separation processes [5, 6].

In particular, the selective separation of cobalt(II) and nickel(II) has been a continuing problem. There have been many studies done [4, 5, 6] and most of them involved the use of organic extractants; however, these are volatile and hazardous solvents that often pose environmental problems in their disposal. Hence the development of a simple membrane extraction system that can separate these metals from aqueous solutions without the need for organic solvents would be an innovative solution to the removal of metals from the industrial wastewater that is a byproduct of such processes. It would also be advantageous if such a system had only a few steps to facilitate the selective separation process.

The decision for the selection of the PVC/Aliquat 336 membrane that was used for the extraction and separation of the three metals was made on the basis of research of the literature [22, 23, 24, 25, 26, 27. 28], for a simple system that did not involve the use of organic solvents. Such solvents are not only expensive, but also hazardous and environmentally unfriendly with regard to their disposal [6, 13]. Other systems that were considered included membranes made from a blend of polymers, but this was rejected as being more specific for rate controlling and medical purposes such as for drug delivery rather than a simple system for metal ion extraction and separation. The PVC/ Aliquat 336 membrane has already been proven effective for the extraction of single transition metals such as cadmium, palladium and gold from hydrochloric acid [22, 23, 29]. PVC is extremely inexpensive, environmentally friendly and can be recycled and when combined with the plasticiser Aliquat 336 it forms a stable, flexible and strong membrane with the Aliquat 336 combining with the long chain PVC so that it is effectively entangled with the PVC. This system is also very simple, in that the extraction can be done in aqueous acidic solutions and the back extraction can be achieved using deionised water. It is proposed that the separation and the extraction of these metals can be done by adjusting the anion concentration of the aqueous acidic solution. The conditions were determined from the examples of other more complex systems that are cited in the literature review [12, 17, 30, 31, 32, 33.34] as will be shown in the work.

1.7 Thesis Overview

The aim of this work was to study the membrane extraction of three transition metals: cobalt, nickel and iron in aqueous media with the ultimate aim to effect their selective separation from each other in a variety of aqueous acidic solutions that included, chloride, sulphate and nitrate anions.

Chapter Two contains a literature review that explores the common types of liquid membranes and common types of extractants that have been used for the extraction of these metals from various media. The literature review continues with a closer look at previous studies that have been done on the extraction of cobalt. nickel and iron in chloride, sulphate, nitrate and cobalt in oxalate media and thus providing a point of comparison for the extraction of the metals from both monovalent and divalent anionic acidic solutions and then examines the separation of these metals in these same aqueous solutions.

Chapter Three explains the methods that were used in the experimental work as well as how the chemical analysis for the determination of chloride, sulphate, nitrate and oxalate ions in solution and back extraction studies (metal stripping) was carried out. It further records the preparation of the solutions that were used in the extraction and separation work and details the preparation of the membranes required for the membrane extraction studies. This section includes information on the changing of the counter-ions in the membrane for the studies done in chloride, sulphate, nitrate and oxalate media.

Chapter Four contains the full investigation of the membrane extraction of cobalt, nickel and iron in various concentrations of aqueous chloride, sulphate, nitrate and oxalate. Back extraction (metal stripping) studies are shown and a preliminary discussion for the nature of the extracted species is presented. This is supported with evidence from studies using Ultra Violet spectroscopy (UV) which was used because transition metal complexes commonly exhibit absorption bands in the UV /visible region of the spectra. These result from the energy differences in the *d*-electron states arising from the electron interactions of coordinated donor atoms and can provide a useful tool for the identification of the complexes that are formed, particularly for the chloro- complexes of cobalt and nickel.

Experience from these single ion studies was used to achieve the selective separations of cobalt from nickel, the reverse selective separation of nickel from cobalt, and ultimately introducing a third metal iron and then selectively separating cobalt from nickel and iron, nickel from cobalt and iron and iron from cobalt and nickel in all of the media previously described.

This membrane extraction system for trace metals is registered under Provisional Patent No 2007900692 titled “Separation of Cobalt, Nickel and Iron in aqueous Solutions”, which is presented for the first time in Chapter Five.

Chapter Six reflects on the experimental findings and looks at the possible areas of future development and work with this membrane extraction system.

Chapter Two

Literature Review

2.1 Historical review

There has been much written about the foundation studies of membrane transport, particularly in reference to the pioneering work of early botanists and cell physiologists. This work is relevant to the present investigation in that while these studies were focused on developing an initial understanding of the mechanisms of the transport of gases and liquids across semi-permeable barriers, they underpin current approaches to metal extraction techniques using membranes.

One account of the early history of membrane transport which was reported in a review by Mason [14], highlights the early work done with pig bladders and illustrates some of the misconceptions relating to membrane transport which was not fully understood in the early years. In these early experiments, a portion of a pig's bladder that had been submerged in water was used to cover a jar of 'wine spirits' and it was observed that the water flowed through the bladder into the wine faster than the leakage of wine spirits to the extent that the bladder would sometimes burst. This was the earliest conscious observation of osmosis, where water moved across a semi-permeable membrane from a region of high water concentration to low concentration.

Oddly, no more work on this phenomenon was done for another 80 years, until French physiologist Henri Dutrochet investigated various membranes and solutions, and he is thought to be responsible for the earliest studies on the role of the membrane [14]. The unstructured nature of this area is illustrated by the fact that a study of the escape of hydrogen from a cracked jar was the next reported study. In later work, Thomas Graham wrote of the nature of diffusion and this was further developed by Adolf Fick who was responsible for Fick's Law of Diffusion [14]. More systematic studies were introduced by van't Hoff using a semi-permeable membrane, and these observations indicated that a dynamic equilibrium state involving concentration difference was reached with such membranes which could be described by thermodynamic principles, whereas with a membrane that physically leaks, the equilibrium reached is due to completely uniform mixing [14].

2.1.2 Contemporary studies of membrane function

More recent work has suggested that the role of a membrane is determined by its particular characteristics and properties such as its composition, permeability and structure, and of especial interest to this investigation is that these characteristics and properties are influenced by extractants that can be introduced into the membrane. As an example, polysulfone membranes that have had an aerosil (pure silicon dioxide) introduced in to the skin of the membrane, will markedly influence the permeability and retention characteristics of the ultra filtration characteristics of the composite membrane [35, 36].

Further, membranes that are prepared from blends of polymers have also attracted much interest. Blends can be used for a wide range of applications, and technology has advanced to the stage where membranes can be designed for specific uses. One such example of ‘designer membranes’ utilises the swelling properties of membranes that are made from both water soluble and water insoluble polymers. These systems can be used in a context where there is need for a rate-controlled compound release situation from the membrane, for example in time-release drug delivery *in vivo*. Our understanding of this reverse-phase morphology phenomenon, is that the blend of extractant and membrane is immiscible, and the membrane, which is the major phase of the blend is homogenously dispersed in the continuum of the minor phase [37]. This idea has been further supported by the examination of the membrane using scanning electron microscopy (SEM) and X-ray diffraction (XRD) [37] which showed the differences in the number and sizes of pores formed, which is thought to have an important effect on the membrane’s activity.

In other studies, membranes that were prepared from blends of poly(acrylic acid)-graft-poly(vinylidene fluoride) with poly(N-isopropylacrylamide) have also been examined using XRD. Also, the morphology of the membranes were observed using SEM in order to investigate physical factors that could affect the permeability of the membrane. These results showed that the membranes were multi-stimuli-responsive and, that they exhibited a strong and reversible pH and temperature dependent permeability to aqueous solutions [38].

The molecular weight of polymers and the molar mass of cellulose acetate membranes has been shown to affect the morphology of the membrane and their separation characteristics [24]. This understanding arose from electron micrographs that suggested that the molar mass of cellulose acetate influenced the membrane which was denser and there was less interconnection between the membrane voids in the fractionation [24]. This was of interest as the membrane that was to be used in the extraction and separation studies was composed of high molecular weight polyvinylchloride (PVC) and the extraction efficiency, which depends on the membrane structure, was an important factor in the specific selection of membrane.

The characteristics and morphology of the membrane seems to play an important role in extraction as these may affect the way in which extraction occurs, the design of the membrane and the type of extractant that is used, all of which can affect rate controlling characteristics [39]. It was found that with increasing pH there may have been enhanced electrostatic repulsion between the negatively charged membrane and the aqueous acid phase which may reduce the efficiency of extraction. Some membranes can exhibit strong and reversible pH and temperature permeability to aqueous solutions [40] that also has a significant effect on extraction. Reverse morphology is exhibited in membranes when blends of polymers are combined and there is the possibility of the exchange of phases between the polymer blends where the minor component forms the continuous phase and the major component the dispersed phase [37].

Much has been written in the literature about the effects of temperature and pH on the stability and performance of membrane extraction studies [14, 25, 40, 41] which suggests that the membrane selected for the membrane extraction studies must be stable at a range of temperatures and pH. This strongly indicates that the membrane selected for this project must also be extremely stable and functional under similar conditions.

The poly(vinyl)chloride (PVC)/ Aliquat 336 membrane that has been used in the membrane extraction experiments in this study can be described as an ”entangled” membrane as it is believed that the Aliquat 336 molecules, that acts as a plasticiser, becomes entangled with the PVC polymer chains in the polymer matrix. It has already been shown that the extraction of metals using this system is dependent on the loading of the Aliquat 336, but this does not explain how the diffusion process occurs [26] and is a ‘gap’ which should be addressed in future work.

More recently, the surface properties and membrane morphology of the PVC/Aliquat336 membrane have been investigated using scanning electron microscopy and atomic force microscopy [42, 43]. Studies were carried out with scanning electron microscopy of a cross section of the membrane that was obtained by freeze-fracture. It was proposed that the increase in extraction rate of cadmium(II) observed in this system is linked to the formation of microstructures in the membrane film that are likely to be micro-channels [42]. Atomic force spectroscopy allowed study of the electrochemical properties of membranes, as well as the morphology and surface “roughness” in membranes [27, 44, 45]. The most likely reason for the surface “roughness” is that it is simply due to the exposure of one side of the membrane to air as it was prepared in a glass dish, whilst the other side is smooth. It has also been suggested that the Aliquat 336/PVC membranes have micro channels in the membranes that facilitate the transport of the Aliquat 336 molecules and metal complexes when the Aliquat 336 is at a level between 30 and 40% [42].

2.1.3 Common types of liquid membranes

The next section of this Chapter contains a chronological overview of the types of liquid membranes that have been used for the extraction of metal ions from aqueous solutions and includes emulsion liquid membranes, bulk liquid membranes, supported liquid membranes, hollow fibre membranes and polymer liquid membranes. This review has been carried out in order to assess the best system to be selected for this project. In addition, the types of membrane transport processes such as cation transport and anion transport mechanisms are discussed and the extractants that have been commonly used in the extraction process are reviewed, because this information will be important in the attempt to achieve optimum extraction efficiency. The classes of extractants included are neutral or solvating agents, organic acid extractants, chelating agents and ion-pair extractants. The last section looks at the literature relevant to the extractive properties of membranes and is followed by a review of some of the work that has been done for the membrane extraction and separation of cobalt (II), nickel (II), iron (II) and iron (III) in aqueous media.

There are a number of types of membrane systems that may be used in the solvent extraction process, and depending upon the species to be extracted, the choice of membrane is crucial in order to maximize the extraction of the metal ions of interest. This is particularly so in the case of trace metal ions, such as those found in wastewaters [9, 20]. In addition, it is essential to be able to effectively strip the metal ions from the membrane using the minimum amount of expensive solvents.

The following sections illustrate and describe the main types of membranes that have been used for metal ion extraction in order to justify the selection of the most efficient system to be used.

2.1.3.1 Emulsion liquid membranes

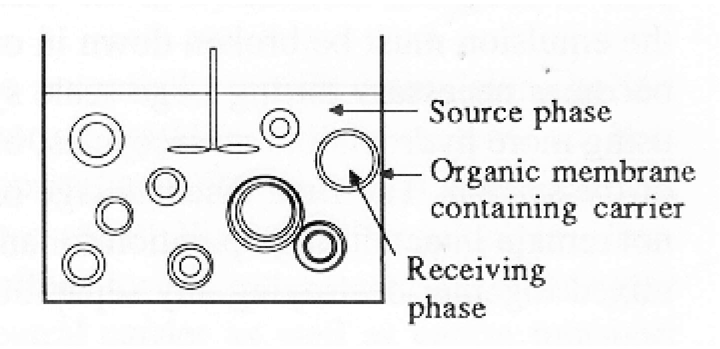


Figure 2.1. Emulsion liquid membrane [46]

Emulsion liquid membrane separation systems such as that depicted in Figure 2.1 above, are made by emulsifying a liquid internal receiving phase in an immiscible organic liquid membrane phase and dispersing this emulsion in the aqueous source phase. Droplets of the emulsion are maintained in the source feed phase using agitation [47]. The first such system was reportedly used in 1968.

Other examples of emulsion liquid membrane systems include electrostatic pseudo liquid membranes (ESPLIM) that were used for the extraction and separation of cobalt and nickel [48], and liquid emulsion membranes (LEM) [49, 50, 51]. Emulsion liquid membranes are typically very thin and have a very large surface area per unit of the source phase volume, which enhances the transport rate. When the organic emulsion phase is added to the larger volume source phase, the concentration of the receiving phase increases.

Whilst one advantage of this system is that the membrane and carrier need only to be slightly hydrophobic or the carrier can be proton ionizable on the surface of the membrane to maintain the stability of this system, there are some disadvantages associated with emulsion liquid membranes. The stability of the membrane can be affected by changes in pH or the ionic strength of the feed phase and the emulsion membrane needs to remain intact during the extraction process. These are two common problems associated with the emulsion liquid membrane in solution [52]. Swelling and leakage in the emulsion liquid membrane systems are studied in a paper by Pfeiffer *et al.* who studied the effects of surfactant concentration, osmotic pressure, internal phase volume fraction and external vessel stir rate and it was found that all of these variables had an effect on the leakage and swelling of the membrane system[47]. Stripping of the metal ions occurs via the addition of a stripping solution, such as ammonium thiocyanate [50].

A decision was made not to utilize this system because of the problems associated with the membrane, such as swelling and leakage of the membrane and the use of toxic and environmentally unsustainable solvents that would be required for the extraction processes.

2.1.3.2 Bulk liquid membranes

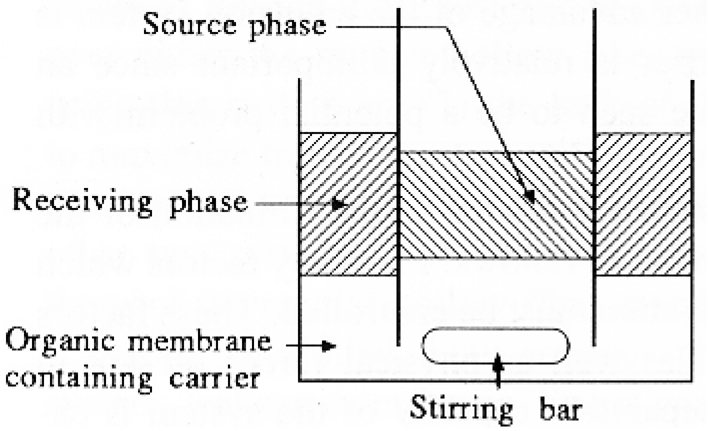


Figure 2.2. Bulk liquid membrane [46]

Bulk liquid membranes (BLM) as shown in Figure 2.2, have also been studied in some detail the earliest studies being in the late 1970’s and 1980’s [52, 53]. The organic membrane phase, typically chloroform, may contain a carrier (extractant) such as tri-n-octylamine (TNOA) that is placed on the bottom of the cell. The two less dense aqueous phases are placed on top and the system is constantly stirred. The stability of the membrane is maintained as long as the stirrer speed is not too high. A bulk liquid membrane was used in a study of the transport of cadmium (II) ions from an aqueous chloride source feed solution to an ammonium acetate strip solution by He *et al.* [29]. The amount of the species of interest was determined by the change in concentration of the receiving phase. This bulk liquid membrane is particularly useful for the transport of anionic and neutral species because the metal ions and H^+ are co-transported. An example of such a membrane is cited in an article by Leon and Guzman [54] which describes the facilitated transport of Cu(II) ions through liquid membranes containing CYANEX 272, D2EHPA, or LIX 984N as carrier and H^+ as counter ions. The carrier diffuses from the bulk membrane phase to the feed membrane interface, where copper(II) ions are exchanged for protons. The copper(II) carrier complex formed diffuses through the membrane to the membrane product interface, where protons are exchanged for copper(II) ions, which are released into the product phase. The carrier is regenerated, thus beginning a new separation cycle [54].

This type of membrane was not selected because it was thought that firstly, a more robust system would be more practical and secondly, it was thought that a system that did not have a need for the transport of neutral species would be more efficient.

2.1.3.3 Supported liquid membranes

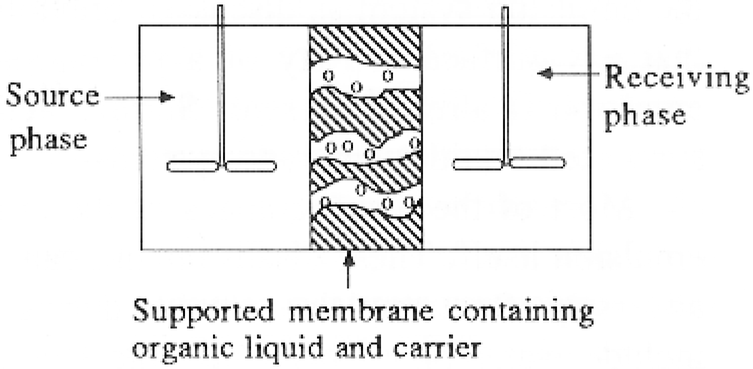


Figure 2.3. Supported liquid membrane [46]

Figure 2.3 shows one of the simplest membrane systems which is a thin sheet of supported liquid membrane (SLM) which was first used in 1986. This membrane is usually made of polymer and the pores are filled with an organic phase and carrier, which is placed between the receiving phase and source phase, both of which are gently stirred. The main disadvantage of supported liquid membranes is the slow leaching of the membrane liquid phase into the receiver and feed solutions, thus reducing its lifetime. Whilst these membranes are ideal on a laboratory scale, there are difficulties in scaling them up for industrial use. Supported liquid membranes have been used for the extraction of cobalt [55, 56, 57] and the separation of cobalt and nickel ions [58, 59, 60, 61]. The organic solvent used in the supported liquid membrane is there only to solubilise the extractant, thus a minimum amount is required. Therefore, unlike solvent extraction the toxicity and also the disposal of the organic solvent is not an issue, however it is the level of selectivity for various metal ions and the stability of the supported membrane remains a significant problem.

2.1.3.4 Hollow fibre supported liquid membranes

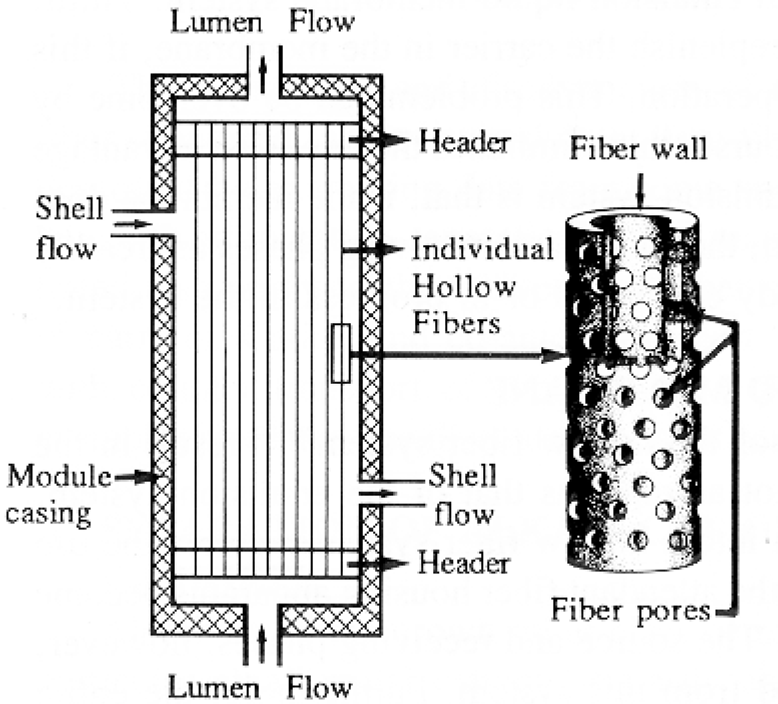


Figure 2.4. Hollow fibre supported liquid membrane [46]

The most recent extraction studies include hollow fibre membranes [15, 16, 17] an example of which is shown in Figure 2.4. The hollow fibre system, which was developed in 1999, can be thought of in terms of a large cylinder with an outer nonporous shell. Inside the shell there are numerous thin fibres running lengthwise whose pores are filled with the organic phase and the carriers (extractants). The feed phase is piped through the system and the receiving phase is forced through the side of the shell.

This system has advantages in that there is little loss or leakage, there is a large surface area for rapid transportation and the feed and receiving phases are easily recovered. However there are also some disadvantages such as the high capital cost, contamination of the membrane, pore fouling and the requirement for a very hydrophobic solvent for metal ion recovery, which is also an environmental issue.

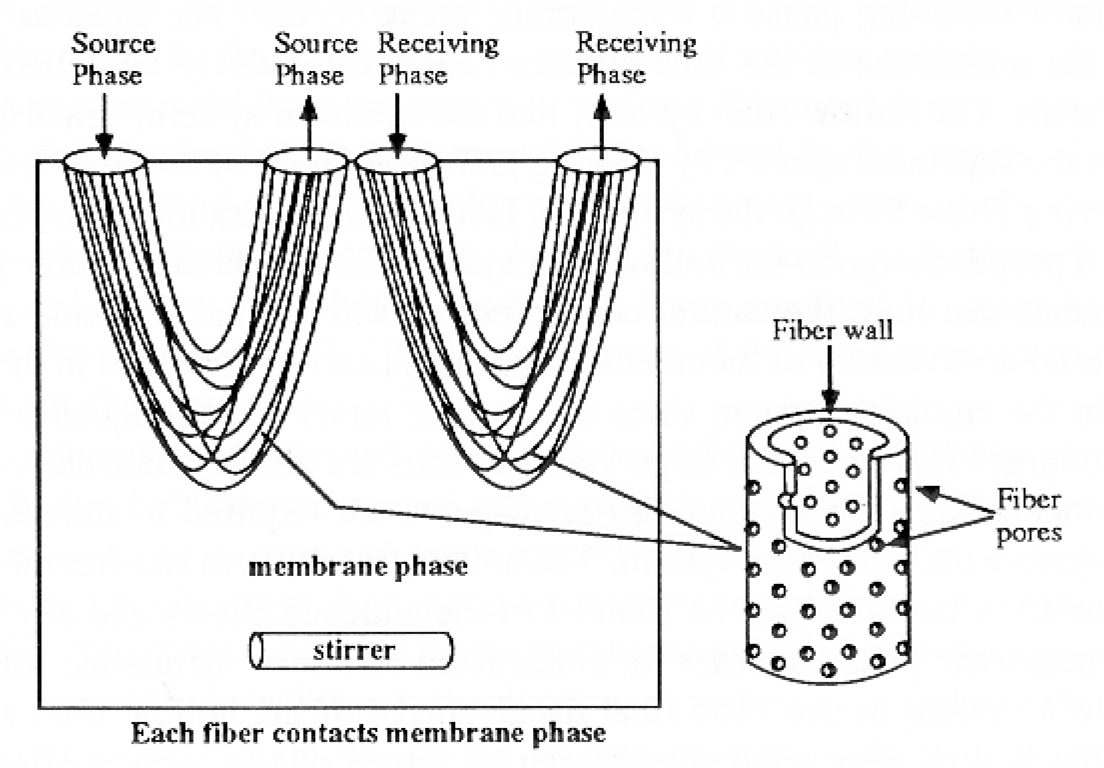


Figure 2.5. Two module hollow fibre supported liquid membrane [46]

A further development of this system is seen in the two- module hollow fibre system shown above in Figure 2.5, where the feed phase is piped through one channel and the receiving phase through another. This system has the advantage of the simple continuous replacement of the lower hydrophobic solvent and a relatively high transport rate, whilst the creation of a boundary layer may be slow. The fouling of the system however, is still a definite problem.

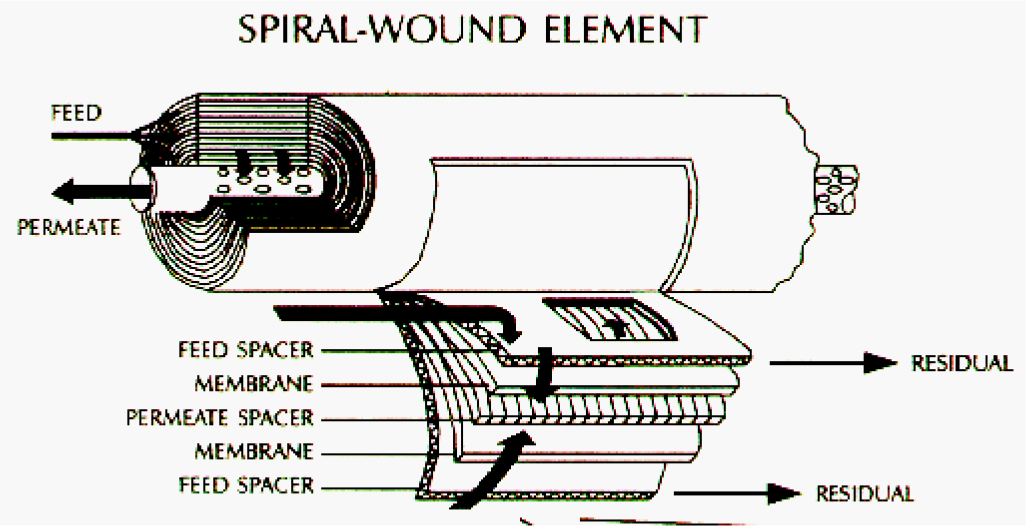


Figure 2.6. Spiral wound membrane [46]

The spiral wound membrane in Figure 2.6, is essentially a flat membrane sandwich, wrapped around a perforated tube, through which the effluent diffuses out of the membrane. The sandwich is actually four layers, a membrane, a feed channel, another membrane, and a permeate channel, which forces all the separated material towards the perforated tube in the center [51].

The possible use of this system was ignored because of the prohibitive cost on a laboratory scale, and because of the complexity of the design, it has a high possibility of fouling of the membranes.

2.1.3.5 Polymer liquid membranes

The other main type of membrane is the polymer liquid membrane, which was developed on the late 1980s, or polymer inclusion membrane [29, 62, 63, 64, 65. 66]. The polymer (a long chain, high molecular weight PVC) is mixed with the liquid extractant Aliquat 336 to form the polymer liquid membrane. This membrane can be described as an “entangled” membrane, because the Aliquat 336, which is used as the extractant, acts as a plasticiser and its molecules become entangled in the polymer matrix with the polymer chains of the poly (vinyl) chloride. Polymer inclusion membranes have been used for the extraction and removal of heavy metals such as chromium from wastewater in the textile industry and industrial wastewaters such as those from the electroplating industry and these have been reported in a paper by Fontas *et al*. [65]. Polymer inclusion membranes have also been used in the extraction and transportation of metal ions and small organic solutes and are proven to have greater stability than other membrane types. A comprehensive summary of the current knowledge of this system was reported in a review by Ngheim *et al*. [66].

Whilst there are some basic problems that are fundamental to such solvent and membrane extraction processes including the loss of solvent, minimal separation and the disposal of the solvent, the polymer liquid membrane appears to combine the ease of use of supported liquid membranes while substantially reducing the loss of the liquid components. Such a membrane extraction process using a polymer supported liquid membrane forms the basis of this work that involves the selective separation of the three transition metals cobalt, nickel and iron in aqueous media.

2.2 Liquid membrane transport phenomenon

To more clearly understand the way in which the extraction occurs in the membrane it will be important to examine the current theories of transport phenomenon and thus information will then be able to be used to postulate the way in which the mechanism of extraction takes place.

There are four basic types of transport systems, each of which has its own mechanisms and carrier types. The four systems are cation transport, anion transport, neutral guest transport and switchable transport. However, in each of these systems, regardless of the mechanism the complexes that are formed must maintain charge neutrality [46]. This section will be restricted to cation transport and anion transport because of their relevance to the project.

2.2.1 Cation transport

Cation transport can occur in either of two ways, and these are known as symport or antiport, as shown in Figures 2.7 and 2.8 respectively. In the symport configuration, a neutral carrier (I) moves the metal ion (M^+) and co-transported anion (X^-) together across the membrane. This occurs in four stages. If the outer side of the membrane is in contact with Aqueous Phase I (AQ. I), and the inner side of the membrane is in contact with Aqueous Phase II (AQ. II), then

1. At the AQ. I interface of the membrane, the metal ion salt is complexed with the carrier.
2. That complex diffuses across the membrane.
3. The release of the metal ion salt occurs at the AQ. II interface of the membrane.
4. The carrier diffuses back across the membrane, ready to continue.

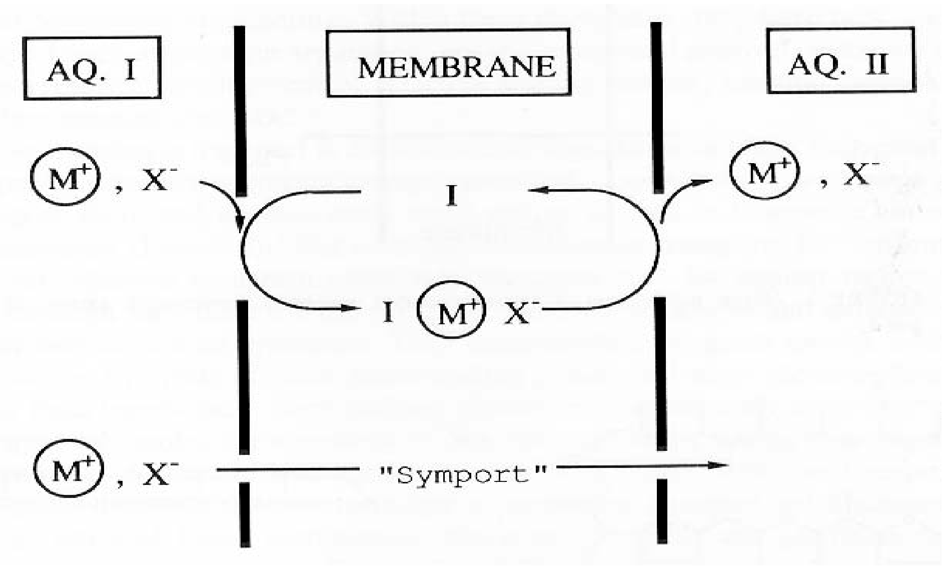


Figure 2.7. Cationic Symport.[46]

For the antiport transport, an anionic carrier (I^-) is used, so these four stages differ.

1. At the AQ. I interphase, the carrier forms a neutral complex with the metal cation.
2. The ion-pair diffuses across the membrane.
3. Cation-exchange reaction releases the metal cation to AQ. II.

4. The carrier complex with the counter-transported ion diffuses back across the membrane.

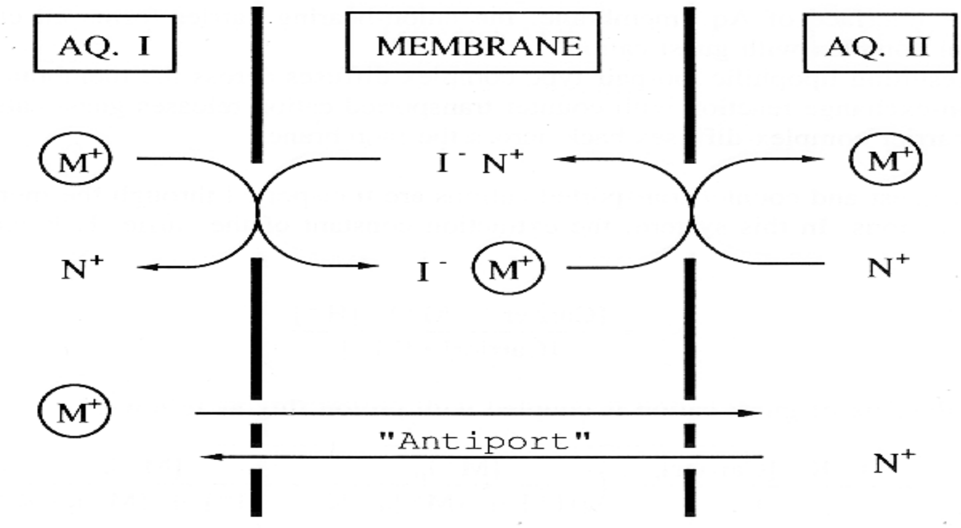


Figure 2.8. Cationic Antiport.[46]

2.2.2 Anion transport

As can be seen in Figure 2.9, anionic transport is similar in mechanism to that of the cationic transport, except for the use of a cationic carrier (I^+) in place of the anionic carrier in the antiport configuration and where S^- is the salt anion.

For the antiport transport, a cationic carrier (I^+) is used and cationic carrier and co-transported anion X^- form a neutral complex in the membrane as does the cationic carrier and metal salt anion (S^-). These anions diffuse across the membranes from Aqueous Phase I and Aqueous Phase II where they are in solution.

For the symport transport the metal cation and salt anion diffuse across the membrane from the Aqueous Phase I and form a neutral complex with the cationic carrier and then the metal cation and salt anion diffuse across the membrane to the Aqueous Phase II.

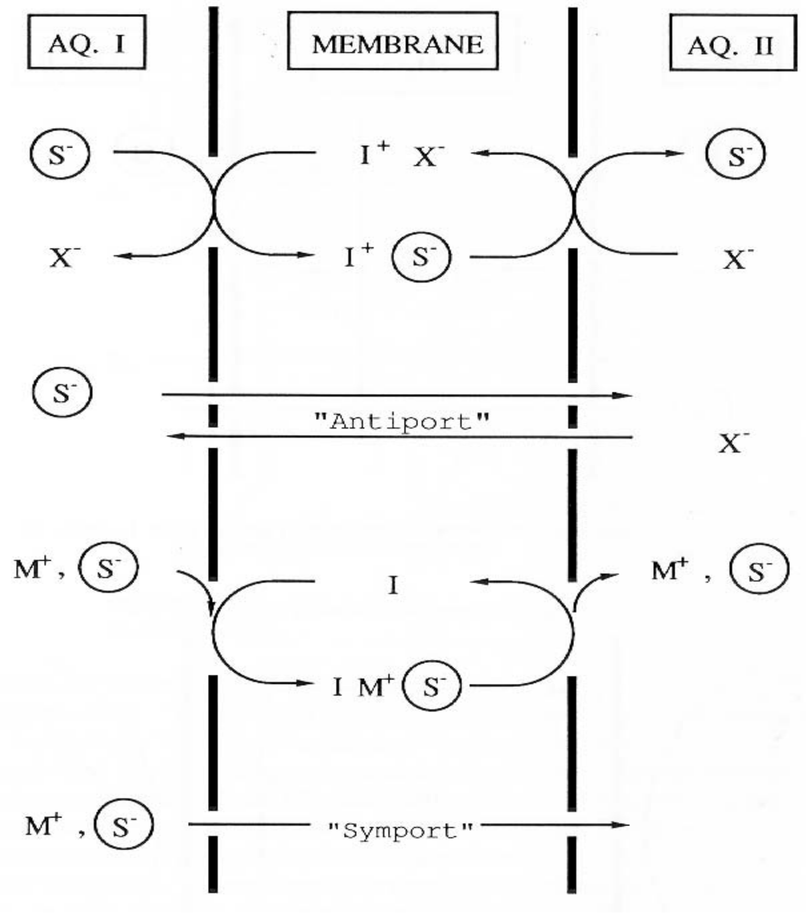


Figure 2.9. Anionic Antiport and Symport Transport [46].

The mechanism of the extraction that will be postulated and discussed in Chapter Four will be linked back to this section in the discussion

2.3 Extractants

For metal ions to be concentrated in an organic liquid phase during the separation process, a carrier or extractant must be added to the aqueous phase to alter the structure of the metal complex and, consequently, its solubility characteristics between the aqueous and organic phases. In the context of this work, there are four basic classes of metal extractants, and in the following discussion these four classes are compared and contrasted on the basis of (i) their chemical structure, (ii) their extraction chemistry, and (iii) the metal species that can be extracted using these systems [65]. These four classes are chelating agents [30, 68, 69], ion-pair extractants [22, 23, 63, 64], neutral or solvating extractants [30, 68, 69], and organic acid extractants [71-75], and the selection of the particular extractant to be used plays an important role in the efficiency and specificity of the extraction of the metal ions [65], which is of special relevance to this project.

2.3.1 Neutral or solvating extractants

Neutral or solvating extractants are large organic molecules which form relatively stable adducts with metal ions. Examples are given in

Figure 2.10 (a) trioctylphosphine oxide and Figure 2.10 (b) tributyl phosphate, ketones and alcohols [20, 30, 68, 69].

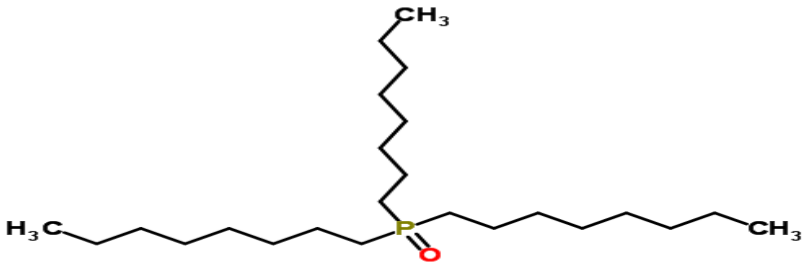
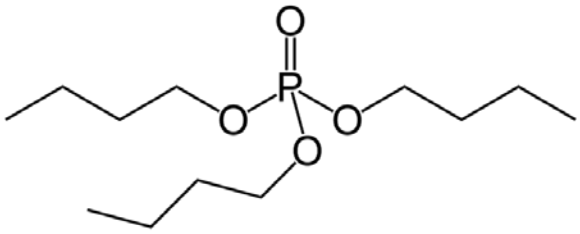


Figure 2.10 (a)

Figure 2.10



(b)

Figure 2.10. Chemical structure of (a) trioctyl phosphine oxide and (b) tributyl phosphate.
Adduct formation can be represented by the following equation for the extraction of uranium, where $(RO)_3PO$ represents the extractant molecule.

$$2(RO)_3PO_{(org)} + UO_2(NO_3)_2 \Leftrightarrow UO_2(NO_3)_2\ 2(RO)_3PO_{(org)}$$

These reactions are kinetically fast and the resultant neutral metal complexes can be extracted using organic solvents. However, the selectivity is low and the organometallic complex must be soluble in an organic medium. Stripping can be done using concentrated nitric acid. However, because the metal extraction that will be investigated in this project will not involve the use of organic solvents, this class of extractant will not be used.

2.3.2 Organic acid extractants

The second category contains organic acid extractants such as phosphonic acids, sulphonic acids, carboxylic acids and phosphoric acids (e.g. di-(2- ethylhexyl) phosphoric acid as shown in Figure 2.11 [70, 71].

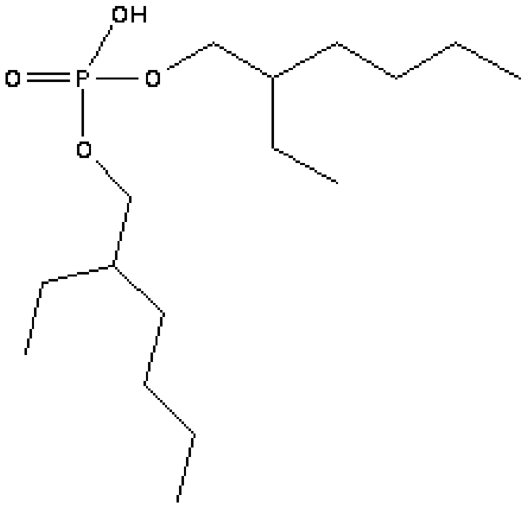


Figure 2.11. Chemical structure of di-(2- ethylhexyl)phosphoric acid

The extraction chemistry is shown in the following example where an adduct is formed:

$4RH_{(org)} + Zn^{2+} \Leftrightarrow R_2Zn \, . \, 2RH_{(org)} + 2H^+$

Phosphonic acids are widely used in the extraction of cobalt and involve commercial extractants such as Cyanex 272 [72-74]. Carboxylic acids can be used for the extraction of copper and nickel and di-(2-ethylhexyl) phosphoric acid can be used to extract a wide variety of metals. The selectivity is often poor and careful pH control is required to achieve reasonable metal separation. For this reason, these extractants were not chosen as being a viable method of selective metal extraction for this project.

2.3.3 Chelating agents

In general, chelating agents have a stereochemical structural arrangement, which involves multiple electron pairs that are geometrically arranged in such a way as to be available for simultaneous bonding with charged metal ions. Examples of interest to this investigation include ketoximes and salicylaldoximes, which have the following structure:

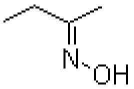


Figure 2.12 (a)

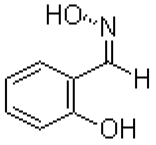


Figure 2.12 (b)

Figure 2.12. The chemical structure of (a) methyl ethyl ketoxime and (b) salicylaldoxime

There are electron pairs available in these molecules (N**:** and **:**OH) that are capable of assuming a cage-like structure around the metal ion to produce a stable metal complex. Cobalt and nickel are typical metal ions that are capable of forming chelates with ketoximes and salicylaldoximes. The resulting chemistry behind the extraction process with this class is summarised in the following equations, where $M(H_2O)_n^{2+}$ represents the aquated metal species which is soluble in aqueous solution, $RH_{(org)}$ represents the chelating agent, and $R_2M(org)$ the metal chelate that is more soluble in an organic phase.

$$2RH_{(org)} + M(H_2O)_n^{2+} \Leftrightarrow R_2M(org) + 2H^+ + nH_2O$$

From the equation above it can be seen that ketoxime and a salicylaldoxime extractants operate on a hydrogen ion cycle, suggesting that stripping of the metal ion from the chelate can be achieved by alteration of pH in a reaction that is the simple reverse of the chelating process. Common commercial oxime-based extractants are LIX^R 984N, LIX^R 622N [31, 75-78] and Acorga M5640 [79], and these are the main commercial extractants that have been used for the extraction of copper [31].

Reported uses of this system for the separation of cobalt and nickel from aqueous acidic sulphate media have been given by Cerpa *et al.* [79], and in this application, the yield of Co and Ni exceeded 90% and the stripping of cobalt and nickel was almost quantitative [79]. However, the efficiency of processes based upon metal chelate extraction are therefore sensitive to acid levels [31] and because of the particular nature of the solvent/extractant characteristics, are very selective for particular metal species [31] and are not appropriate for use in this project because of their toxicity.

2.3.4 Ion pair extractants

This class of extractants includes, primary amines, RNH_2 [80, 81], secondary amines R_2NH , tertiary amines R_3N [13, 20, 83, 84], and quaternary ammonium salts $R_3R'N^+Cl^-$ [20, 22, 23, 63, 64].

The extraction chemistry of quaternary and tertiary amines are described by the following equations in which M^- represents the negatively charged aqueous metal complex, for example $CoCl_4^{2-}$:

$R_3R'N^+_{(org)} + M^- \Leftrightarrow R_3R'N^+M^-_{(org)}$ Equation 1

$R_3N_{(org)} + H^+ \Leftrightarrow R_3NH^+_{(org)}$ Protonation Equation 2

$R_3NH^+ + M^- \Leftrightarrow R_3NH^+M^-_{(org)} + H^+$ Equation 3

The use of these compounds in practice is usually in the form of a commercial preparation such as the mixture of quaternary ammonium salts (Aliquat 336), whose application to the extraction of cobalt in aqueous acidic solution is represented by the following equations, where ACl represents Aliquat chloride:

$2ACl + CoCl_4^{2-} \Leftrightarrow A_2\,CoCl_4 + 2Cl^-$ Equation 4

or

$ACl + CoCl_3^- \Leftrightarrow A\,CoCl_{.3} + Cl^-$ Equation 5

This class of compounds is useful for the extraction of a number of heavy metals including uranium, cadmium, palladium, cobalt and gold because the ion pair compounds are relatively

stable, the kinetics of extraction and stripping are fast, and stripping can be conveniently carried out using Milli-Q water [30, 63, 64, 66]. However, as indicated earlier, the extraction usually involves a negative anion complex such as $CoCl_4^{2-}$, and, in general, selectivity is high. Further, Aliquat 336 is not pH dependent, but rather dependent upon the concentration of the chloride anion. It has been found [13, 20] that quaternary and tertiary amines are more selective than primary and secondary amines in this regard.

This system was selected for this investigation as the Aliquat 336, when combined with the PVC, is recyclable and there is no need for the involvement of organic solvents in the separation or extraction.

2.4 General review of membrane extraction and separation studies

2.4.1 Extraction studies of cobalt, nickel and iron in aqueous media

As indicated in an earlier section, cobalt, nickel and iron are transition metals that share many similar properties and are often found together in nature or in commercially important processes. The efficient extraction and separation of these metals has been a problem that has perplexed chemists for decades, and consequently there have been many examples of solvent extraction studies of these metals that have been carried out in a variety of aqueous and acidic media. In this section, some of the work involving the extraction of cobalt(II), nickel(II), iron(II) and iron(III) from aqueous media is reviewed, describing the advantages and disadvantages of these early approaches.

For convenience, this section has been subdivided into extraction studies of these three transition metals from aqueous (i) chloride, (ii) sulphate, (iii) nitrate and
(iv) oxalate media.

2.4.1.1 Extraction of cobalt in chloride media

There are several studies discussed below which exhibit good results when using different types of membranes and extractants, and it was on the basis of the observations made with these studies that a system was selected and refined for this study.

Emulsion liquid membranes have been used for the recovery and extraction of cobalt(II) using naphthenic acids as the carrier in kerosene as the membrane material [82]. Increased cobalt(II) concentration was found to be extracted with increased molarity of HCl when Cyanex 923 was used as extractant in toluene [74, 84]. This indicates that increasing chloride ion concentration is a factor, and that the nature of the extractant is critical. It was also found that the leaching capacity of Cyanex 923 was good and it was easy to recycle and strict control of the phase variables was unnecessary [74, 84]. In another study, liquid-liquid extraction of cobalt(II) in chloroform using calix[4] resorcinarene membrane and an aqueous liquid phase is shown to be more effective with increased acidity [52]. The pH value and the nature of the supporting salt in the accepting phase were important factors in controlling the extraction and transfer processes [31]. When the chelating resin Dowex M-4195 containing the bis(2-pyrimidylmethyl)amine functional group had been used to extract cobalt(II) in concentrated chloride solutions [85], it was shown that the adsorption of the metal ions increased with increased pH, as the resin becomes protonated [85]. This paper was useful in that it suggested that by adjusting the chloride concentration the metal extraction was selective and the information could be used to select optimal experimental conditions. As indicated earlier the use of Aliquat 336 is not pH dependent, but is dependent on chloride ion concentration, so it would be a reasonable extractant to be used for the experimental work.

In a later study that also examined the effect of the chloride ion, the solvent extraction of cobalt(II) in 4.0 M and 7.0 M hydrochloric acid solutions was reported by Paimin *et al*. [86] using Aliquat 336 in chloroform. Further studies have been done using Aliquat 336-TBP (tri-n-butylphosphate) and Aliquat 336-tri-n-octylphosphine oxide in the separation of cobalt(II) and nickel(II) from chloride media showing the ability of cobalt(II) to form quaternary ammonium complexes with the Aliquat 336 [30]. Quaternary ammonium

salts such as Aliquat 336 (tri-n-octylmethylammonium chloride) and amines including Alamine 336 and Alamine 308 have been commonly used as extractants of cobalt(II) from chloride solutions, where tetrahedral complexes such as $CoCl_4^{2-}$ are usually formed. These complexes that are formed with Aliquat 336 occur more readily with cobalt(II) than any other transition element except for zinc(II) [1], which suggests the use of this extractant for the current project.

Having established the importance of the chloride ion concentration and the complexes that are formed and that can be extracted, the third area of importance is the extractable species. The complex formation following the transport of cobalt(II) through a supported liquid membrane using triethylamine (TEA) as a carrier in the organic solvent cyclohexanone supported by polypropylene polymeric hydrophobic nonporous film [56] was described. It was shown that the metal complexes that were formed in dilute hydrochloric acid (HCl) of 1M and 3.75M were the protonated TEA molecules that were attached to ($CoCl_3^-$) and ($CoCl_4^{2-}$). The possible mechanism was also discussed in the paper [56]. It was concluded that the species responsible for the transport of Co ions are LH. $CoCl_3^-$ and LH2.$CoCl_4^{-2}$, ie. protonated TEA (LH) molecules attach to the ($CoCl_3^-$) and ($CoCl_4^{2-}$) anionic species. This was relevant to this study, in that it suggested the nature of the extracted species that could be expected in these separations. It was therefore assumed that this transport will show similarities to those involved with the complexes that are formed in the extraction studies that will be discussed in Chapter Four.

2.4.1.2 Extraction of nickel in chloride media

Early anion-exchange studies on the system Ni(II)-HCl-Dowex-1 showed that nickel did not appear to be adsorbed as readily from concentrated hydrochloric acid solutions when compared with other transition metals [87]. However the chelating resin Dowex M-145 was later found to be useful for adsorbing Ni(II) from concentrated chloride solutions [88]. The adsorption of nickel was found to increase with pH as the resin became deprotonated [88], indicating that the effect of pH is an important factor in the extraction of nickel(II) and its ability to form chloro-complexes. The determination of the effect of pH on concentrated chloride solutions such as those found in nickel electroplating baths was studied to enable more efficient

control of the electroplating bath composition and to improve the plating characteristics using sequential injection analysis [17].

Further support for the selection of the acid concentration was found in a paper that discussed extractants which included: Alamine 336, Alamine 308 and Aliquat 336 and are commonly used for nickel extraction from chloride solutions [89]. Early liquid-liquid extraction studies that used Aliquat 336 as an extractant in benzene as the organic phase and Ni(II) and a range of concentrations of hydrochloric acid from 1M to 10M were carried out. It was found from these studies that the nickel ion failed to be extracted in any of the higher hydrochloric acid concentrations, and was only extracted at the lower level. This information was useful as a guide to the acid concentration necessary for the successful extraction of nickel in aqueous chloride solutions [33].

The kinetics of extraction and back extraction of nickel using dodecylsalicyloxime (HDSO) as extractant with hexane as the organic phase were studied and the nickel complexes formed used as a basis for determining the mechanism of extraction[88]. Back extraction can be described as the "stripping" of the metal ions from the membrane. The extraction of nickel ions in chloride media was carried out using aldoxime extractants such as 2-ethylhexanal oxime (EHO) in dodecane in the presence of sodium chloride and nitrate to determine the effect of pH and chloride concentration on the extractability of Ni(II) ions [90] and the extracted species formulated. Further studies by the same group proposed a kinetic mechanism for pH greater than 4 for the formation of an alternative complex [91].

Although organic phases will not be used in this project, the results seen here are of interest, because of the concentration of HCl that was used in these studies. These findings will act as a guide in the investigation. Also, the nature of the complexes that were reported to have been formed in these works may be similar to the conditions used in this study.

2.4.1.3 Extraction of iron in chloride media

Dowex – 4195 is a macroporous polymer with a polystyrene–divinylbenzene matrix

on to which the weakly basic chelating bispicolylamine has been attached creating a tertiary amine [85]. This was used in the extraction studies of some transition metals including iron(III) in 3.6M hydrochloric acid [85]. Iron(III) complexes that were extracted with EDTA over a pH range of 2-5, and also extracted by solutions of Aliquat 336 in 1,2-dichloroethane were reported in early liquid extraction studies that were carried out by Irving *et al.*[92]. The solvent extraction of Fe(III) using tertiary alkyamines in kerosene was found to be effective at low pH in extracting the Fe(III) in to the kerosine organic phase [34].

The effect of chloride concentration on the extraction of iron(III) was also studied when an emulsion liquid membrane was used for the recovery of iron(III) from groundwater. It was found that the recovery of the iron(III) from the external feed phase increased with the addition of hydrochloric acid at concentration of 2-3M and decreased with the addition of sulphuric or nitric acid in the internal phase [92]. In addition, it was found that the subsequent demulsification was unsatisfactory but this was improved with the addition of 1.5M sulphuric acid to the hydrochloric acid at a ratio of 3:2 [93]. Iron(II) was extracted using Alizarin Red S with Aliquat 336 in chloroform at a pH exceeding 4.2 M [94]. It has been demonstrated that iron(III) which can be found in mineral pregnant leaching solutions or industrial wastewater streams, can be extracted using N,N'-dimethyl-N,N'-diphenylmalonamide and N,N'-dimethyl-N,N'-diphenyltetradecylmalonamide in acidic chloride media such as hydrochloric acid at concentrations higher than 3M [95, 96].

Other studies that examined the extraction of iron(III) included the use of Cyanex 923 as the mobile carrier with an immobilized liquid membrane for the extraction of iron(III) with hydrochloric acid in the feed phase [68]. In a later study mono(2-ethylhexyl)phosphoric acid in *n*-hexane was used as the organic phase with Fe(III) in HCl as the aqueous phase, and it was found that at 0.5M HCl the Fe(III) was able to be extracted [97]. Similarly, iron(III) could be extracted in hydrochloric acid with maximum extraction occurring at concentrations higher than 2M HCl using Aliquat 336 as the liquid ion-exchanger [33, 98]. These papers were useful in that they gave an indication of the possible range of chloride and acid concentrations for which iron(III) could be successfully extracted. Of special interest were the studies that used Aliquat 336 as extractant, which will be used in this investigation. Unfortunately there was no information on the extraction of iron(II) from chloride solutions.

Clearly, the use of Aliquat 336 as extractant has merit as it has been successfully used for the extraction of cobalt(II), nickel(II) and iron(III) from chloride media.

These studies indicated that the membrane extraction of Co(II) and Ni(II) were most likely to occur at high concentrations of chloride for cobalt(II) and low concentrations of chloride in the case of nickel(II). The membrane extraction of Fe(III) was most likely to occur with a chloride concentration midway between that required for the extraction of the Co(II) and Ni(II). The use of Aliquat 336 as the extractant was also an important consideration because the membrane extraction of these metals will not be dependent upon the pH of the aqueous media, but rather the chloride concentration of the aqueous chloride media. This is because the Aliquat 336 forms an “ion-pair” compound with the “metal chloride complex”. Whilst not all of these studies appear to be relevant to the work in this thesis they do provide a very good indication of the chloride concentrations that are likely to be most effective for the membrane extraction and separation of Co(II), Ni(II) and Fe(III) in chloride media.

2.4.2 Extraction of cobalt in sulphate media

The work in this thesis will explore the membrane extraction of cobalt, nickel and iron in sulphate media. In many industrial processes cobalt is extracted from ores by leaching with ammonia followed by sulphuric acid that is sometimes combined with nitric acid, which may leave significant concentrations of sulphate and nitrate ions [2, 3, 4].

Emulsion liquid membranes with polyethylene glycol (PEG) as a bi-functional surfactant (extractant and emulsifier) were used for the extraction of cobalt(II) in sulphate media. Equilibrium experiments were conducted at different concentrations of PEG at a constant pH of 2.0. The extraction rate was quite high due to the large interfacial area of the emulsion globules [48]. Organophosphoric acids such as D2EHPA (di(2-ethylhexyl) phosphonic acid) and organophosphinic acids such as Cyanex 272 are commonly used as extractants for the extraction of cobalt(II) from sulphate solutions [89]. Supported liquid membranes

containing Celgard^R and hybrid liquid membranes were used with D2EHPA, Cyanex 272 and Cyanex 302 for the transport and extraction studies of cobalt(II) in sulphate solutions [58]. It was shown that the metal cations were extracted faster with the supported liquid membrane than with the hybrid liquid membrane [58]. A Goretex S10187 teflon membrane was used for the support of the organic phase with D2EHPA as the carrier in kerosene, which was incorporated into the supported liquid membrane by capillary action, and the aqueous feed solution contained cobalt sulphate [59]. These details were relevant to the project because this paper provided an example of extraction where a supported liquid membrane was used and a similar membrane will be utilized in this project.

Permeation experiments were performed in order to ascertain the effect of stirrer speed and carrier concentration on the metal ion transport. It was found that at low stirring speeds, the permeation rate of metal ions was controlled mainly by the aqueous film diffusion, but at high stirring speeds the permeation rate was controlled by aqueous film diffusion and the membrane diffusion [99]. In further studies where Cyanex 272 was the carrier, some good results for the recovery of cobalt in sulphate solutions using liquid-liquid extraction were obtained where metal recovery from spent portable batteries was studied [99]. The extraction from sulphate media using liquid surfactant membranes have also been reported using Cyanex 272 as the extractant [100]. The experiments were carried out at a temperature of 50^{o}C and it was found that at low concentrations of the carrier the recovery of cobalt was low. However, with an increased concentration of Cyanex 272 the metal recovery improved [100]. In more recent studies, hollow fibre supported liquid membranes were used containing D2EHPA diluted in kerosene as a carrier with promising results [101], whilst the non-dispersive liquid –liquid extraction of cobalt(II) in sulphate media using a hollow fibre membrane with Cyanex 272 and Ionquest 801 as extractants were found to yield good results compared with previous studies for the removal of metal ions from dilute wastewater [102]. Liquid-liquid extraction using D2EHPA in hollow fibre membrane have also been successfully studied [103]. Liquid surfactant membranes using Cyanex 302 as carrier has been used to show high extractability for cobalt(II) in synthetic leaching liquor [104]. The pH of the external phase was found to have a profound effect on the liquid surfactant membrane process and the best results were obtained at an approximate pH of 4.1. Cyanex 302 was also found to have a higher extractability for cobalt than Cyanex 272, possibly because of the higher acidity of Cyanex 302. Temperature increases favoured the permeation kinetics, but it was thought that the membrane breaking up at higher temperatures could potentially be a problem. [104].

The formation and suggested cobalt complex that is formed was found in a paper that used a supported liquid membrane with D2EHPA as extractant and this system was used for the extraction of cobalt(II) in sulphate solution with Celgard 2500 membrane as solid support [50]. The kinetics of permeation are studied and the model presented considers the aqueous layer diffusion of cobalt ions toward the membrane, the chemical reaction between Co(II) and D2EHPA at the feed membrane interface, and the membrane diffusion of D2EHPA and its Co(II) complex [55].

2.4.3 Extraction of nickel in sulphate media

The most common extractants used for the extraction of nickel by solvent extraction in sulphate solutions include carboxylic acids, organophosphoric acids such as D2EHPA , phosphoric acids such as PC-88A and Ionquest 801, dithiophosphonic acids such as Cyanex 301 and ketoximes such as Lix 87QN and Lix 84 which are used to extract nickel from ammoniacal solutions [91]. A study of the extraction of nickel from ammoniacal sulphate using 5-dodecylsalicylaldoxime in kerosene using a vibro-mixer type continuous extractor has generated some very promising results [87]. The increased interfacial area and surface renewal rate were thought to be the reasons for the increased extraction rate constants that were obtained as compared with those obtained in the Lewis type transfer cell extraction [87]. Organophosphoric acid and phosphonic acids with aldo- and ketoximes were also studied with regard to the efficiency of extraction of nickel and the effect on the kinetics of extraction [88]. The extraction of Ni(II) in Cyanex 301 using different solvents that included: n-hexane, chloroform, cyclohexanone, xylene, toluene and kerosene as the organic phase and 5M sulphuric acid in the aqueous phase were examined and showed high extraction efficiency and recovery from electroplating bath and spent catalyst residue[17]. Mixtures of pyridinecarboxylate esters and nitro- alkylsalicylic acids were used in the solvent extraction studies of nickel from weak acidic solutions with extremely good results [105].

The mechanism of nickel transport through a supported liquid membrane containing D2EHPA as the mobile carrier has been investigated and a permeation rate equation derived by taking into account the diffusion of the ions through the aqueous boundary layer adjacent to the membrane [59].The extraction of nickel with EDTA by solutions of Aliquat336 chloride in 1,2-dichloroethane was achieved and stated as a function of the pH of the aqueous solution in very early extraction studies [92]. In another study of the formation of aqueous nickel sulphate complexes, synthetic wastewater containing nickel sulphate in strong acid was examined and a chemical model analysis was carried out for the aqueous complexations with sulphonic resins such as Purolite NRW-100 using glass jacketed columns [10]. It was found that more than 94 percent of the nickel was recovered [10].

These papers provided the basis of what acid concentrations might possibly be used for the extraction of nickel and the possible mechanisms that may be relevant for the extraction processes that will be postulated as part of the project.

2.4.4 Extraction of iron in sulphate media

Extraction of iron(III) from aqueous sulphate solutions was presented in a paper where a primary amine, Primene JMT, in benzene with octan-1-ol was used as the extractant [106]. The extraction of Fe(II) and Fe(III) as a function of the sulphuric acid concentration was shown as was the extent of the extraction when thiocyanate was added. Following this extraction the species that were involved in the mechanism were postulated [107]. The presence of iron(III) in sulphated leach liquor was examined and it was found that most of the iron(III) can be extracted at a pH of 2.25 [16]. In a separate study, the use of Cyanex 272 in kerosene was used for the extraction of iron(III) from aqueous acidic sulphate media, sulphuric acid being in the aqueous phase at relatively low pH [108]. Liquid-liquid extraction of Fe(III) from sulphate media using Cyanex 272 was achieved at low pH [109].

The extraction of cobalt(II), nickel(II) and iron(III) has been achieved in sulphate media using a range of extractants of which the most commonly used are from the phosphonic acid group. However, the extraction of these metals has not been done using Aliquat 336 as the extractant, nor has it been done using an Aliquat

336/PVC membrane. The extraction of these metals also was found to be dependent upon the pH of the solution as has been shown in previous studies. The use of a quaternary ammonium compound such as Aliquat 336 with a changed counter ion of the quaternary ammonium compound is not pH dependent, but is dependent upon the sulphate concentration. One of the aims of this work is to demonstrate the ability of the

Aliquat 336/PVC membrane as a viable tool for the membrane extraction of these metals in a variety of aqueous media.

2.4.5 Extraction of cobalt in nitrate media

This section considers the extraction of cobalt in nitrate media using different extractants with varying extraction efficiency. These included the use of hydroxamic acid (LIX-1104) in chloroform which was used to study the extraction of radioactive cobalt in nitrate media. In addition the chelating properties in this system were also determined [110]. The use of a supported liquid membrane containing an organophosphorous extractant mono-2-methylhexyl ester (PC-88A) dissolved in n-dodecane showed high permeability and selectivity for the cobalt ligand complexes. [60]. The extraction and separation of cobalt(II) from solutions containing both
cobalt (II) and nickel(II) using a liquid surfactant membrane was achieved using LIX 84, Lix 860 and Lix 65 N as extractants, where it was found that cobalt(II) was extracted faster and preferentially over the nickel(II) ions [111]. Aliquat 336 was also used as extractant for Co(II) and it was found that as the concentration of Aliquat 336 increased, the extraction efficiency decreased [112]. Transition metal thiocyanate complexes were found to be adsorbed on various solid polymers such as cellulose acetate involving the association of cationic complexes with the ammonium ion and the anionic metal thiocyanate complex [113]. In addition the extractant D2EHPA dissolved in toluene has been used as an extractant for the separation of cobalt(II) from manganese(II) at a pH of 3.0, which gave satisfactory extractability [114].

Supported liquid membrane technology has proven to be a useful tool for the extraction of metals such as cobalt(II) using organophosphoric compounds as extractants in waste water [113]. Poor extractability was shown using the extractant Cyanex 923 in toluene [74]. The membrane that is to be used in this study will be

a polymer supported liquid membrane, and these results suggest that the use of a different extractant may produce better results.

2.4.6 Extraction of nickel in nitrate media

A feasibility study was done on the treatment and recycling of wastewater in a nickel plating plant using flat sheet membranes from different manufacturers which included polyamide composite membranes, polysulphone membranes and polyacrylonitrile hollow fibre modules. It was found that the polysulphone support membrane was susceptible to solvent attack and the feed pH had an effect on nickel rejection [98, 115]. This paper provided an indication of the possible concentration range of nitrate and hydrogen ions for nickel extraction in nitrate media.

2.4.7 Extraction of iron in nitrate media

The extraction of Fe(III) from a soil sample using the Tessier method [116] and nitric acid was successfully used by Cave *et al.*[116]. The extraction of Fe(III) in 0.7M nitric acid can be achieved using Dowex-50-W-X8 columns [117]. Other examples of processes that have been used for the recovery of iron in solution include the use of trioctylphosphine oxide (TOPO) in decane as extractant, that was used for the recovery of Fe(III)from 0.1-1M nitric acid solutions [66] and the solvent extraction of iron(III) from nitrate media using bis(2-ethylhexyl)phosphonic acid in hexane. It was found that the iron(III) could be extracted in the concentration range of 2.0 - 4.5M and stripped from the organic phase using 0.75M nitric acid [118].

2.4.8 Extraction of cobalt in oxalate media

Oxalates are strong complexing agents and are often found in wastewaters, but few solvent extraction studies have been done with regard to cobalt metal extraction from aqueous media containing oxalate. Some work was done using Aliquat 336 in chloroform [86] and more recent studies have been done on the modeling of the metal-ligand interactions of the Co(II)-oxalate system in high ionic strength sodium chloride solutions with organic ligands such as EDTA [118]. The Co(II) formed Co(II)-oxalate ligands as well as

cobalt tetrachloro-complexes with the presence of more highly concentrated chlorine solution (5M sodium chloride)[119]. This study was chosen to compare the extraction of cobalt(II) in a divalent acid solution.

2.5 Separation of cobalt, nickel and iron in aqueous media

Separation technology is of growing importance as our natural resources become depleted; in addition there are water scarcity problems and increased pollution concerns, particularly with regard to the disposal of organic solvents, extractants and the pollution resulting from waste water that may be contaminated with heavy metals. Hence, it is imperative that new methods for metal extraction and separation need to be found and tested.

The role of separation processes can be described as “enabling technologies” and these and other issues are discussed in a paper by Sikdar *et al*. [13] who also outlines some common environmental problems and opportunities for the introduction of separation technologies and applications of membrane technology [13].

There are many examples of such membrane technology that are used for the separation, removal and recovery of potentially harmful metals and metal ions from industrial wastewaters such as those produced in the metal finishing industry. For example, chromium(VI) which is toxic to humans and other organisms [120], electroplating rinse waters and wastewaters that contain nickel, which is both toxic and carcinogenic and in which some of these may be removed by strong acid [10]. Another example is the separation of cadmium and nickel from rechargeable batteries in highly concentrated acidic leaching solutions using membrane-assisted (hollow fibre membrane) and solvent extraction [121]. However, selective separation of cobalt(II) and nickel(II) has been an existing problem for many years, because they are most commonly found together with iron in laterite ore. There have been many studies done and a number of them involve the use of organic extractants which are volatile and hazardous solvents that can often pose environmental problems in their disposal. Hence the development of a membrane extraction system that can separate these metals from aqueous solutions without the need for organic solvents is an innovative and timely solution to the removal of metals from industrial wastewater that is a product of such processes.

There has been much research that has been done and although many relate to solvent extraction, the parameters of these studies will provide useful information for the extraction and separation studies that will be shown in this project.

Some of the most common methods used for the separation of nickel and cobalt by solvent extraction from laterite and sulphide leach solutions are reviewed in a paper by Cheng *et al*. [4] who discuss the advantages and disadvantages of the processes currently being used. The existing nickel laterite processes can be divided into three main categories: sulphide precipitation, hydroxide precipitation and direct solvent extraction processes. Of these processes the disadvantages of the first two are that they are very complicated, with high capital and operational costs and the metal recovery may be low as well as the fact that they are environmentally unfriendly due to the use of hydrogen sulphide and ammonia gases. The direct solvent extraction processes are much simpler, less expensive and have fewer environmental concerns as well as producing a high metal recovery, and are seen as a step toward membrane extraction. The use of membrane extraction processes is seen as having the greatest potential in the future provided that a highly selective, stable, environmentally friendly and inexpensive extractant can be found.

The following section reviews some of the current extraction processes that have been studied for the separation of cobalt, nickel and iron in aqueous media, in order to assist in the development of parameters and procedures for the investigation. The section has been subdivided into the separation of these metals in chloride, sulphate and nitrate media.

2.5.1 Separation of cobalt, nickel and iron in chloride media

Chloride based refining was successfully pioneered by Falconbridge in 1953 who developed a matte treatment process using chloride acid leach to separate nickel from nickel-copper-cobalt mattes. With the development of solvent extraction, the matte leach process using hydrochloric acid and tertiary amine salts meant that the cobalt could then be extracted into an organic phase. Observations made on the role of chloride metallurgy, where the nickel sulphide concentrates can be treated and nickel solubilisation can be achieved with HCl/O_2 leach, are discussed in a paper by Van Weert [122].

The separation of cobalt(II) , nickel(II) and iron(III) from scrap alloy involves four main steps: (i) pyrometallurgical pretreatment, (ii) electrolytic dissolution, (iii) separation through solvent extraction and (iv) electrolytic recovery of the metals [34]. According to Aue *et al*. the most efficient technique for the selective separation of Fe(III), Co(II) and Ni(II) in chloride solutions is the use of tertiary alkylamines such as Alamine 336 in kerosene. Using this technique it was found that at low chloride concentrations the iron(III) could be extracted into the organic phase while cobalt(II) and nickel(II) were not affected, and at high chloride concentrations the cobalt(II) is extracted but not nickel(II) [34]. Another multi step process can be seen with the separation and extraction of iron(III), cobalt(II) and nickel(II) from scrap alloy. This was investigated using a four step process, one of which included separation by solvent extraction of the cobalt(II) and nickel(II) in chloride solution and Alamine 336 in kerosene [34]. The system did have some problems including maintaining a homogenous organic phase during separation [90]. Further separation of cobalt and nickel has been studied using Aliquat 336-TBP (tri-n-butylphosphate) and Aliquat 336-TOPO (triocylphosphine oxide) in the organic phase and the metals in chloride media where the Aliquat 336 concentration was kept constant and the TBP and TOPO concentrations varied [30] In this work it was found that the Aliquat 336-TOPO system achieved better separation results [30].

The separation of iron(III), cobalt(II) and nickel(II) in aqueous halide media using Aliquat 336 in benzene was the subject of a paper [98] and the range of acidities investigated were 0.1-10M hydrochloric acid (HCl). It was found that the Ni(II) was not extracted over the acidity range and around 85% of the Co(II) was extracted at 8M HCl and Fe(III) was extracted at concentrations higher than 2M [98]. Polyurethane foam loaded with Aliquat 336 has also been used to separate iron, cobalt and nickel and also cadmium from aqueous halide acid solutions [98]. It was found that nickel(II) and cobalt(II) showed no extraction in the range of 1 - 8M HCl, however cadmium(II) and iron(III) were extracted into the foam. The cadmium could be extracted in the whole range of acidities, whilst the iron(III) extraction was achieved at a concentration of greater than 2M HCl [98].

Other studies that considered the effect of hydrogen ion and acid concentration were carried out in order to optimize the conditions for the extraction and separation of the metal ions. These included the extraction of various metals including Fe(III), Ni(II) and Co(II) as their anionic complexes with EDTA by solutions of Aliquat 336 chloride in 1,2-dichloroethane. They were studied as the function of pH of the aqueous phase and it was found that iron(III) was separated from many other metals in strongly alkaline solution [92].

Other papers that looked at optimization factors included a study of the separation of cobalt(II) and nickel(II) using micellar ultrafiltration with micelles containing mono-ethylhexyl ester. The effects of pH and concentrations of the surfactant and applied pressure were examined, but the solvent extraction did not show high separation [123]. In a separate study, where Cyanex 923 was used as the extractant in kerosene to separate cobalt(II), nickel(II) and some other transition metals from hydrochloric acid media showed promising results. It was found that the extraction and separation was dependent upon the pH of the media and the concentration of the extractant. With increasing concentration of Cyanex 923, better extraction of the metal ions was found [74]. Separation studies of cobalt(II) and nickel(II) by ion-association with a crown ether (dicyclohexyl-18-crown-6) in nitrobenzene and ion-association from 0.05M potassium thiocyanate 1M hydrochloric acid was established and back extraction of the cobalt in 1.0M nitric acid was successfully achieved [124] indicating that the separation may be achieved at low acid concentration.

A more recent study used an organic phase containing Aliquat 336 in dodecanol and kerosene and a hollow fibre membrane with a rotating disc to separate and extract cobalt(II) and nickel(II) from concentrated hydrochloric acid solution, but problems were encountered in the stripping phase due to membrane diffusion in the hollow fibre membrane [125].

Membrane studies included emulsion liquid membranes with tri-alkyl-amine hydrochloride in kerosene as extractant in the organic phase that were used in the extraction and separation of cobalt(II) from nickel(II) hydrometallurgical effluent. These investigations yielded good results and the study was able to identify cobalt tetrachloride as the most favourable species for ion exchange in an aqueous solution of 7M HCl [51].

The separation of cobalt, nickel and iron from chloride media using acid leach and aqueous chloride has been reviewed and it has been shown that the extraction of cobalt was possible at high chloride concentrations and nickel and iron at lower concentrations. The anionic complexes were able to be extracted with EDTA by solutions of Aliquat 336 chloride in 1,2 dichloroethane. This suggests that ion association extractants appear to be the most suitable for the extraction and separation of the metals in aqueous chloride media. The use of Aliquat 336 appears to be a sound choice of extractant for the separation and extraction of cobalt, nickel and iron in chloride solution.

2.5.2 Separation of cobalt, nickel and iron in sulphate media

Solvent extraction using LIX 84 as extractant in kerosene as the organic phase and the metals ions to be separated in sulphuric acid solutions in the aqueous feed phase was reported for the leaching of cobalt rich crust where the cobalt(II) remained in the aqueous phase and the nickel(II) could be extracted into the organic phase [76]. LIX 84 was also used in extraction studies of liquid surfactant membranes and it was found that the LIX 84 had a strong chelating affinity for the nickel(II) ions [111].

A two-stage selective precipitation technique was developed for nickel and cobalt separation in sulphated leach liquor of nickel laterite oxide ore [126]. The technique was based on the solubility products of the hydroxides of iron, cobalt and nickel for different oxidation states. The iron was separated at a pH of 2.25 - 2.5 with calcium carbonate. The cobalt and residual iron were separated from the nickel using bleaching powder [125]. Whilst this was not a solvent extraction process *per se*, it was interesting to note that the extractability of each metal was pH dependent [126]. Factors that affected the separation were also reported in a paper that described the use of supported liquid membranes of PTFE film that were soaked in the liquid membrane solution containing 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (HEH(EHP)) in kerosene. Using a predetermined weight ratio and a feed solution of cobalt and nickel in sulphuric acid, this solution

was studied for the simultaneous permeation of cobalt and nickel [61]. In further studies, where a rotating film contactor using Cyanex 302 as carrier was used for the separation of cobalt(II) from nickel(II) by pertraction, it was determined that a higher pH in the feed solutions favoured metal recovery, but the separation ability deteriorated [73].

Again, useful information can be obtained from solvent extraction studies and membrane studies that have been carried out. Emulsion liquid membranes have also been used to recover cobalt(II) from a solution containing both cobalt and nickel sulphate with PX 100 polyamine membranes containing PC 88A with excellent results [127]. Mechanistic studies of the transfer of cobalt(II) and nickel(II) across a supported liquid membrane with D2EHP as carrier have been reported and it was found that the permeation rates of the metal ions were determined by the diffusion of the ion complex and the interfacial solvation reaction that were rate determining factors in the extraction [59].

Similar extractants were used for the separation of cobalt(II) and nickel(II) by solvent extraction using phosphoric, phosphonic and phosphinic acids as extractants in the organic phase and it was determined that the nature and addition of the neutralizing agent is very important in the extraction process [126, 127]. Further studies have been reported using the same extractants to evaluate the separation process on a laboratory scale and also to remove common impurities such as zinc, manganese and calcium from sulphide leaching [125]. This process was extended to a successful small-scale refinery in Cuba [126].

Liquid surfactant membranes were used where the carrier was Cyanex 272 and the surfactant ECA 4360 and Escaid 110 as diluent to demonstrate the separation of cobalt and nickel with lower concentrations of Cyanex 272 [100]. Emulsion liquid membranes containing polyethylene glycol (PEG) have also been used to demonstrate the selectivity of copper, nickel and cobalt [50]. Cyanex 302 as carrier was used in a report on the application of liquid surfactant membranes for the separation of cobalt and nickel in a synthetic leaching liquor where it was found that the selectivity of extraction was heavily dependent on the pH [79]. This is further supported by separations carried out with D2EHPA and Acorga diluted in Exsol D100 [128, 129]. Other studies included supported and hybrid liquid membranes Celgaard 2500) that were used where the commercial extractants D2EHPA, Cyanex 272 , Cyanex 301 and 302 were the ion carriers in kerosene and the aqueous phase contained an equimolar mixture of cobalt and nickel in sulphate metal solutions [58]. It was found that the hybrid liquid membranes showed faster liquid transport and the acidity strongly influenced the transport fluxes of each and in a different liquid-liquid extraction system that used a hollow fibre membrane module with DEHPA in the organic phase to extract a mixture of metals that included zinc, copper, cadmium and cobalt [103].

Separation of cobalt and nickel was also achieved using a hollow fibre supported liquid membrane containing HEH(EHP) diluted in kerosene as the carrier [101]. A mathematical model and numerical simulations were developed for the transport of cobalt in mixtures of cobalt and nickel by a hollow fibre liquid membrane with 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester as a carrier to analyze the permeation rates and separation factor of cobalt and nickel across the hollow fibre supported liquid membrane [130, 131]. An electrostatic pseudo liquid membrane was used for the extraction and separation of nickel and cobalt using a reactor tank filled with the extractant and feed and stripping solutions and it was found that the main variables that affected the extraction and separation were the applied voltage, feed and strip flow rates and pH [48].

The separation of cobalt, nickel and iron in sulphate media can be achieved using a variety of extractants of which the most successful seemed to be commercial chelating agents and organic acids. The separation appeared to be heavily dependent on the acid concentration of the media that was used. Solvent extraction has been used in a multi-stage process for the separation of these metals from ores and acid leaches, but this information does provide a valuable source of material about the conditions and extractants that may be used in the extraction and separation processes. In this project the selective separation and extraction will be carried out using Aliquat 336 as the extractant combined with PVC as the membrane and the process will be completed in aqueous solution without the use of organic solvents.

2.5.3 Separation of cobalt, nickel and iron in nitrate media

Sorption and permeation studies on the behavioural patterns of metal thiocyanate complexes on cellulose acetate polymers formed part of the early work done for solvent extraction and separation of cobalt and nickel [113]. More recent studies reported on the adsorption of copper, nickel and cobalt ions from aqueous solution by methacrylic acid/acrylamide monomer mixture grafted poly(ethylene terephthalate) fibre which showed good selectivity and the increase of adsorption amounts of cobalt and nickel with increasing adsorption temperature [132]. There have been other studies that reported on the effect of temperature on the extraction of these ions in aqueous media with thiourea mono phosphazene in chloroform with similar findings [41].

Early papers reported the separation of iron(III), nickel(II), cobalt(II) and copper(II) from the insoluble aluminum fluoride by leaching with nitric acid, which is described by Jaganathan *et al.* [133]. This group of researchers used graphite furnace atomic absorption spectrometry as the tool for the analysis. The selectivity and separation of cobalt(II) and nickel(II) by supported liquid membranes containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester dissolved in n-dodecane showed that the extraction was dependent on the loading ratios of the extractant [31]. Also reported, was the separation of nickel(II) and cobalt(II) in nitrate media by mixtures of carboxylic acids and pyridine derivatives. The effect on the extraction and separation of these metals was determined, and it was found that by increasing the concentration of the pyridine derivative, the nickel-cobalt separation was increased [134]. The same authors also studied the separation of nickel and calcium in sulphate media with similar extractants [71. 105].

The separation of the three metals has been completed with the use of organic acids in conjunction with chelating extractants in nitric acid and organic solvents which were also used in the solvent extraction process. However, the literature did not shed much light on the separation process with the use of ion-pair extractants, which will be used in this project.

From the literature that has been reviewed, it is clear that the separation of cobalt(II), nickel(II) and iron(III) can be achieved in a variety of media using different extractants and types of membranes. However, it is also clear that there is no single convenient method that can be applied for the separation of these metals using a single membrane extraction system, and achievement of this system is the main aim of this thesis.

Chapter Three

Experimental

3.1 Materials

3.1.1 Reagents

The commercial preparation Aliquat 336 (Aldrich, USA) was obtained as a mixture of quaternary ammonium chlorides and was used as received as the extractant. Alamine 336 (Henkel, USA), didecylamine (Fluka, USA) and decylamine (Fluka, USA) were all used as received and utilized as extractants. High molecular weight poly(vinyl)chloride (Selectaphore Fluka, USA) and Copolymer (Fluka, USA) were used in the membrane preparation. Tetrahydrafuran (THF) was HPLC grade (BDH, UK) and was further purified by passing through an activated alumina column to remove stabilizers and peroxides before being used in the preparation of the membranes. Hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3), oxalic acid ($H_2C_2O_4$), lithium chloride (LiCl), potassium chloride (KCl), sodium chloride (NaCl), calcium chloride ($CaCl_2$), cobalt(II) sulphate ($CoSO_4.7H_2O$), cobalt(II) nitrate ($Co(NO_3)_2.6H_2O$), cobalt(II) oxalate ($CoC_2O_4.6H_2O$), cobalt(II) chloride ($CoCl_2.6H_2O$), nickel(II) chloride ($NiCl_2.6H_2O$), nickel(II) sulphate ($NiSO_4.7H_2O$), nickel(II) nitrate ($Ni(NO_3)_2.6H_2O$), iron(II) chloride ($FeCl_2.4H_2O$), iron(III) chloride ($FeCl_3$), iron(II) sulphate ($FeSO_4.6H_2O$), iron(III) sulphate ($Fe_2(SO_4)_3$), iron(II) nitrate ($Fe(NO_3)_2.6H_2O$), iron(III) nitrate ($Fe(NO_3)_3$), sodium sulphate (Na_2SO_4), sodium nitrate ($NaNO_3$), and sodium oxalate ($Na_2C_2O_4$), were all analytical grade reagents (A.R.), (Ajax, Australia) and used in the preparation of sample solutions.

3.1.2 Preparation of Co(II), Ni(II), Fe(II) and Fe(III) solutions

All the solutions that were prepared are shown in the following Tables 3.1 and 3.2, where “X” denotes the anion concentrations for solutions that contained 100ppm of the metal ion that was used in the experimental analysis.

In this work Milli-Q deionised water (Milli-Q, USA) was used for all solution dilutions.

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Table 3.1
Solutions containing 100ppm of Co(II)

Concentration	HCl	H_2SO_4	HNO_3	KCl	NaCl	LiCl	$CaCl_2$
10M	X						
9M	X						
8M	X						
7M	X					X	
6M	X						
5M	X	X	X	X	X	X	
4M	X						
3.5M							X
3M	X	X	X	X	X	X	
2M	X	X	X				
1.5M							X
1M	X	X	X	X	X	X	X

Table 3.2 Solutions containing 100ppm of Ni(II), Fe(II) and Fe(III)

Concentration	HCl	H_2SO_4	HNO_3	KCl	NaCl	LiCl	$CaCl_2$
7M	X					X	
5M	X	X	X	X	X	X	
3.5M							X
3M	X	X	X	X	X	X	
1.5M							X
1M	X	X	X	X	X	X	X

Co(II), Ni(II), Fe(II), Fe(III), Li(I), K(I), Na(I) and Ca(II) standards for atomic absorption spectrometry were prepared from 1000 ppm spectroscopic standards (BDH Spectrosol) and diluted with Milli-Q deionised water as necessary.

3.2 Apparatus and chemical analysis

The concentrations of Co(II), Ni(II), Fe(II), Fe(III), Li(I), K(I), Na(I) and Ca(II) in feed and back extraction solutions were determined by flame atomic absorption spectrometry (Varian Model Spectra AA 400 spectrometer). The instrumental parameters are shown in Table 3.3 below.

Table 3.3

Instrumental parameters for AAS

Metal	Cobalt	Nickel	Iron	Calcium	Potassium	Lithium	Sodium
Wavelength (nm.)	345.4	341.5	372.0	422.7	766.5	670.8	589.0
Slit width (nm)	0.2	0.2	0.2	0.2	0.5	0.2	0.2
Lamp current (mA)	6	6	**6**	10	6	6	6

The samples were taken directly from the cell system and analysed using AAS. Calibration curves were obtained for all metal ion analysis for standardization and were linear in all cases in the ranges involved in these analyses.

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When deionised water was used as the back extraction solution, the concentration of the H^+ ion was measured potentiometrically (Model B417, Hanna Instruments, USA). The determination of the chloride ion concentration in the back extraction solution was based on direct precipitation titration with a standard 0.010M solution of silver nitrate (Sigma, Australia) and fluoroscein indicator (Fluka, Australia).

Ultraviolet visible spectra of the species involved in the metal ion extraction were done using a Carey Model IE UV Varian spectrometer. Calibration curves for Cobalt(II) and Nickel(II) were prepared from Spectrosol solution and diluted appropriately with Milli-Q deionised water. A clear membrane that had not been used for extraction was used as the standard and the UV spectra were obtained from the membranes that had been used for metal ion extraction.

3.3 Preparation of membranes

The membranes used in this study were prepared by dissolving a mixture of known amounts of Aliquat 336 and poly(vinyl)chloride (PVC) with a total mass of 800 milligram (mg) in 5-10mL of THF. The homogenous solution obtained was then poured into a glass ring on a flat glass plate. The THF was allowed to evaporate slowly over 12 hours to yield a colourless, flexible, transparent and mechanically strong membrane. The membrane was then removed from the glass plate and used for the membrane extraction study. Membranes containing 10, 20, 30, 40 and 50% Aliquat 336/PVC (w/w) were prepared. It was found that membranes of Aliquat 336 content higher than 50% were soft and sticky and mechanically too weak to be used for the extraction experiments [44, 72]. The membranes containing the extractants: Alamine 336, didecylamine and decylamine were all prepared in the same manner as that described for Aliquat 336/PVC and the results for the extraction efficiency with cobalt(II) in HCl are shown in Chapter 4. Another set of membranes was made in the same manner using Aliquat 336 and Copolymer (Fluka, Australia), but these were also very soft and sticky and therefore deemed unsuitable for use.

The membranes had a diameter of 80mm and were found to have a thickness of 252µm., which was measured with a micrometer. The importance of the thickness of the membrane was discussed in a paper by Wang *et al*. [29] where it was suggested that the membrane thickness appears to be an important parameter for determining the metal extraction capacity of the membrane.

3.4 Preparation of Aliquat 336 sulphate, Aliquat 336 nitrate and Aliquat 336 oxalate

In the study of the extraction of cobalt(II) sulphate, the extractant used was required to be converted to the sulphate form, because the Aliquat 336 was supplied in the form of the chloride. The conversion of the Aliquat 336 chloride to the Aliquat 336 sulphate was carried out as follows. A known amount of Aliquat 336 dissolved in hexane was shaken vigorously with a solution of a known concentration of sodium sulphate and left to stand until the formation of three phases. The aqueous layer was separated from the other two phases and analysed for the chloride and the sulphate content by titration with lead nitrate and bromophenol blue indicator [135] to ensure all of the chloride was converted to sulphate on the Aliquat 336. The remaining layers were heated in a water bath (Ratek, Australia) and the hexane was removed by evaporation. The resultant Aliquat336 now had the sulphate counter ion instead of the chloride.

This process was repeated using sodium nitrate and sodium oxalate, thus replacing the chloride in the Aliquat 336 with nitrate and oxalate respectively. As before, the separated solutions were analysed for chloride (Volhard titration method), nitrate (titration by modified Leithe procedure [135]) and oxalate content (titration with potassium permanganate (A.R., Ajax, Australia) [135] respectively. All the analyses were done in triplicate as outlined in the “Handbook of Anion Determination” [135]. It was determined that the percentage purity of the extractant in each case was 99.0 ± 0.1%.

3.5 Membrane extraction studies

Two studies of the membrane extraction were done, the first using a two compartment cell of equal volumes of 200 mL each being filled with a feed phase containing 100ppm Co(II) solution. The compartments were separated by the Aliquat 336/PVC membrane, which was held by Teflon seals adjoining the cells and thermostated at 25 ^{o}C and stirred mechanically with a magnetic stirring bar at a constant rate throughout the experiment. The extraction of the metal was monitored by taking 1.0 mL aliquots from each cell at regular time intervals for analysis by atomic absorption spectrometry. The solution that was removed was replaced each time with an equal volume of fresh solution [22, 23, 26, 28,29, 62, 63, 64].

The second set of studies was carried out in a single cell that contained feed solution only and the membrane which was cut into four equal sections to optimize the exposure of the membrane for maximum extraction of the metal ion that was suspended in solution. The cell was thermostated as previously explained, continuously stirred mechanically with a magnetic stirring bar and the extraction of the metal was monitored in the same manner as has been described above. Each extraction was done three times to ensure the accuracy of the results that were obtained.

The single cell studies showed the same efficiency of extraction of the metal ion. The single cell was used in preference, as it was faster and enabled multiple experiments to be completed at the same time. These results are shown in Chapter 4.

3.6 Back extraction

Back extraction ("stripping") of the metal ion from the membrane was carried out by placing the membrane in 100mL of deionised water (Milli-Q) thermostated at 25 ^{o}C and stirred mechanically with a magnetic stirring bar at a constant rate throughout the experiment. The back extraction of the metal was monitored by taking 1.0 mL aliquots from the cell at regular time intervals for analysis by atomic absorption spectrometry [22, 23, 26, 28, 29, 62, 63, 64,].

Back extraction experiments involving different concentrations of HCl (0 – 5.0 M) in the back extraction solution revealed that the degree of back extraction increased with decreasing concentration of HCl. It was established that deionised water was capable of rapid and quantitative back extraction of the Co(II), Ni(II), Fe(II) and Fe(III) from the Aliquat 336/PVC membranes. Experimental results of the back extractions are shown in Chapter Four. The membranes used in the extraction studies were set aside for further analysis and investigation by UV/visible spectroscopy.

Chapter Four

Membrane Extraction Studies of Cobalt, Nickel and Iron from Aqueous Media

4.1 Introduction

In this Chapter, the extraction of cobalt(II), nickel(II), iron(II) and iron(III) from aqueous media is investigated using membrane technology and the extracted species that are involved in the extraction process is postulated. The studies look at the various extractant species for their interactions with each of the ions and this information is used to determine a membrane extraction procedure that will maximise the efficiency of the extraction process. Whilst previous studies have been carried out with a range of metals including cadmium, copper, gold and palladium in hydrochloric acid media using an Aliquat 336/PVC membrane [22, 23, 26, 28, 29], they did not extract and ultimately separate the three metals (cobalt(II), nickel(II), iron(II) and iron(III)) from a variety of aqueous media. It is possible that this has not been done because there are conflicting extracting mechanisms, resulting in a range of complexing species with the complicating factor that the formation of these various species is often pH dependent. However, in this work it will be shown that the extraction of the species using a quaternary ammonium salt such as Aliquat 336 as the extractant is dependent on the concentration of the anion.

Extraction occurs as a result of the combination of the Aliquat cation R_4N^+ with the anionic species of the metal complexes. Consequently, the efficiency of the extraction is dependent on the availability of the anionic species of the metal complexes and the formation constants of the complex formed between the R_4N^+ of the Aliquat 336 and the anionic metal species. This dependence is demonstrated in this thesis and can be used to explain the mechanism that is involved for each extraction and to determine the species that is involved in the extraction process. The structure of the extracted species for the cobalt and nickel chloride complexes can be identified from studies using UV/Visible spectroscopy.

Extractant function and extractant species identification are the key steps that have been used to systematise this work. These investigations will be carried out using a supported liquid membrane in an attempt to successfully separate and extract the three transition metals individually from a range of aqueous media. It is believed that this will be a unique process for such separation and extraction.

The next section contains a description of the studies carried out for each of the metal ions detailing the extractions that were done in a range of relevant media. Whilst this section appears somewhat repetitive, the detail is important because it provides the key to achieving the selective separation and extraction of the metals that will be shown in the following Chapter. In this complex environment (i) the valency of the metal extractants, (ii) their ability to form suitable complexes with the membrane matrix, and (iii) when there are one or more different metal ions present in solution the dependence of the extraction of each metal on the anion concentration, are critical factors. A detailed knowledge of these variables is necessary for the application of this unique separation and extraction process. Specific data relating to these issues will be shown in Chapter Five where the 40% (w/w) Aliquat/PVC membrane is used for this novel separation and extraction process.

4.2 Results and Discussion

4.2.1 Membrane extraction studies of Co(II), Ni(II), Fe(II) and Fe(III) in chloride media

4.2.1.1 Membrane extractant studies

Comparative membrane extraction studies were carried out using four different extractants; a primary amine (decylamine), a secondary amine (didecylamine), a tertiary ammonium salt (Alamine 336) and a quaternary ammonium salt (Aliquat 336). This was done in order to determine the most efficient extractant for the membrane extraction of the metal ions: Co(II), Ni(II), Fe(II) and Fe(III).

Extraction curves were obtained for the extraction of the 100ppm Co(II) in 7.0M hydrochloric acid, 100ppm Ni(II) in 1M HCl,100ppm Fe(II) and Fe(III) in 3M HCl under the same conditions that were used for the metal ion extraction process, but using the membranes that contained the primary, secondary, tertiary and quaternary ammonium salt extractants that were prepared in the same manner as previously described in Chapter Three. The extraction curves are shown in Figure 4.1 below.

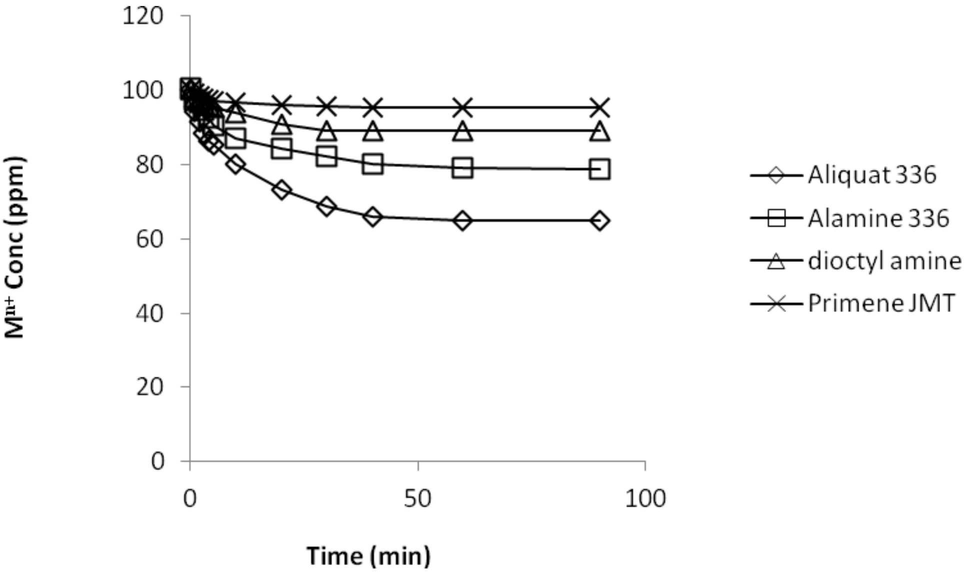

Figure 4.1. Concentration vs. time curves for the extraction of the metal ion (M^{n+}) in HCl using quaternary (Aliquat 336), tertiary (Alamine 336), secondary (dioctylamine) and primary amines (decyclamine (Primene JMT)).

As can be seen from Figure 4.1, the maximum extraction of M^{n+} is seen in the extraction curve for the 40% (w/w) Aliquat 336/PVC membrane and the extractability decreases from the quaternary amine salt, Aliquat 336 to the primary amine, 40% (w/w) decylamime/PVC membrane. This is in accordance with the general observation that tertiary and quaternary ammonium salts are more selective extractants for a metal ion than primary or secondary ammonium salts. Similar extraction curves were obtained for each of the metals M^{n+} that were studied.

Based on the results obtained using the four different amines and ammonium salts, Aliquat 336 was selected as the extractant of choice and the 40% (w/w) Aliquat 336/PVC membrane system was used in all future metal ion extraction studies to attempt to show the versatile properties of this membrane.

4.2.1.2 Efficiency of extraction of the membrane

Two studies of the membrane extraction were carried out, the first using a two compartment cell and secondly, a single cell, as previously described in Chapter Three. These studies were carried out in order to ascertain whether there was any difference in the experimental data obtained for the alternative membrane extractions and to thereby optimize the extraction efficiency and practical procedures.

Further, in an effort to ascertain the region of maximum efficiency of extraction of the membrane, extraction studies were carried out using membranes of 50%, 40%, 30%, 20% and 10% (w/w) Aliquat 336/PVC with a feed solution containing 100 parts per million (ppm) Co(II) in 7.0M HCl. The concentration of hydrochloric acid was selected on the basis of previous experimental studies [79]. As can be seen from the extraction curve shown below (Figure 4.2), the maximum extraction occurred with a membrane containing 50 % (w/w) Aliquat 336/PVC. However as discussed earlier [23, 26] these 50 % (w/w) membranes were found to be impractically soft, so the membranes containing 40% (w/w) Aliquat336/PVC were used for the remaining experimental studies. In addition, it was found that there was no difference in the results (the results for each system were very similar) that were obtained using the single cell and two cell system and these results are shown in Figure 4.2 and Figure 4.3.

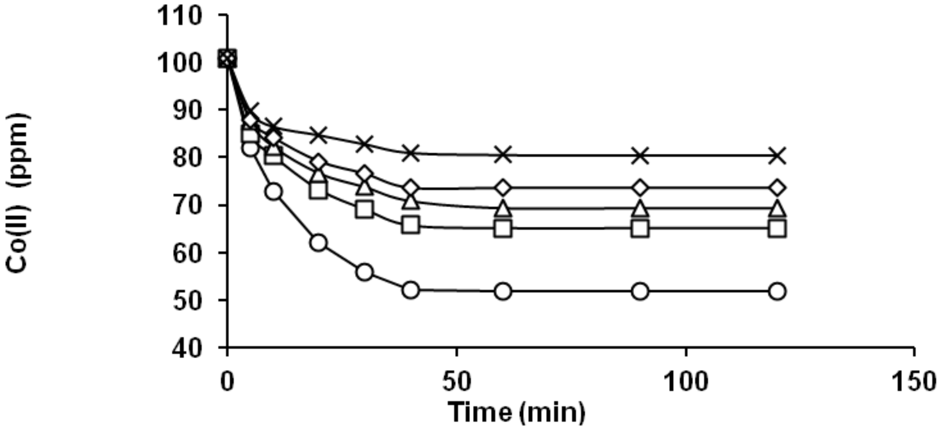

Figure 4.2. Aqueous Co(II) concentration vs. extraction time for membranes containing; 10%(×), 20%(◇), 30%(Δ), 40%(□) and 50%(○) (w/w) Aliquat 336/PVC (feed solution composition: 100 ppm (Co(II) in 7.0 M HCl in single cell system).

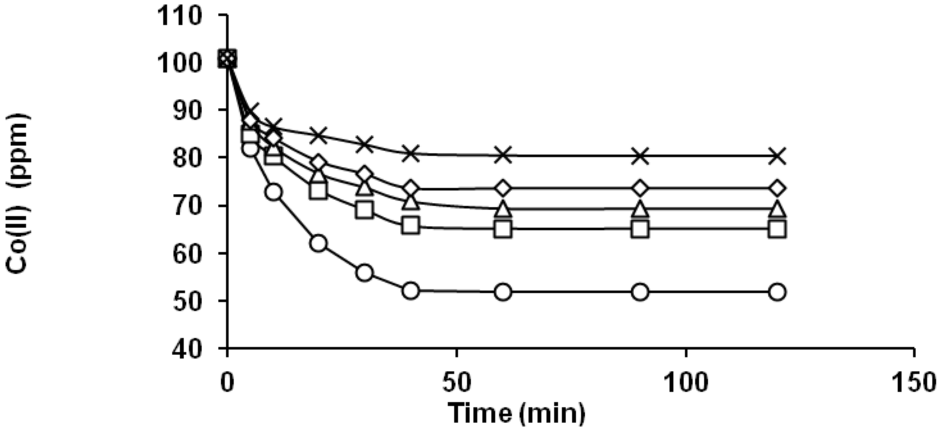

Figure 4.3. Aqueous Co(II) concentration vs. extraction time for membranes containing; 10%(✕), 20%(◇), 30%(Δ), 40%(□) and 50%(○) (w/w) Aliquat 336/PVC (feed solution composition: 100 ppm (Co(II) in 7.0 M HCl in the two cell system).

One very interesting feature of the extraction curves is the rapid equilibration time. As can be seen equilibrium was reached in less than 60 minutes, which was about two orders of magnitude faster than for comparable PVC based solid-phase absorbent systems studied, where extraction was conducted from solutions of lower hydrochloric acid concentration [64].

4.2.1.3 The influence of hydrochloric acid concentration on the efficiency of membrane extraction of Co(II)

The concentration of hydrochloric acid in the feed solution was found to substantially influence the extraction of Co(II) into the 40% (w/w) Aliquat 336/PVC membranes. Equilibrium between the membrane and the feed solution was established for all concentrations of HCl studied (1.0 – 10.0 M) after the first 60 minutes of extraction yielding the results reported in Figure 4.4.

In this Figure the dependence of the fraction of Co(II) extracted at equilibrium as a function of the HCl concentration in the feed solution is demonstrated. The amount of Co(II) extracted increased substantially as a result of increasing the hydrochloric acid concentration from 1.0 to 7.0 M , a result similar to that in the solvent extraction of Co(II) into chloroform solutions of Aliquat 336 chloride [86]. Further increases in the HCl concentration past 7.0 M resulted in insignificant increases in the amount of Co(II) extracted, thus the

optimal concentration of HCl for the extraction of Co(II) was selected as 7.0 M.

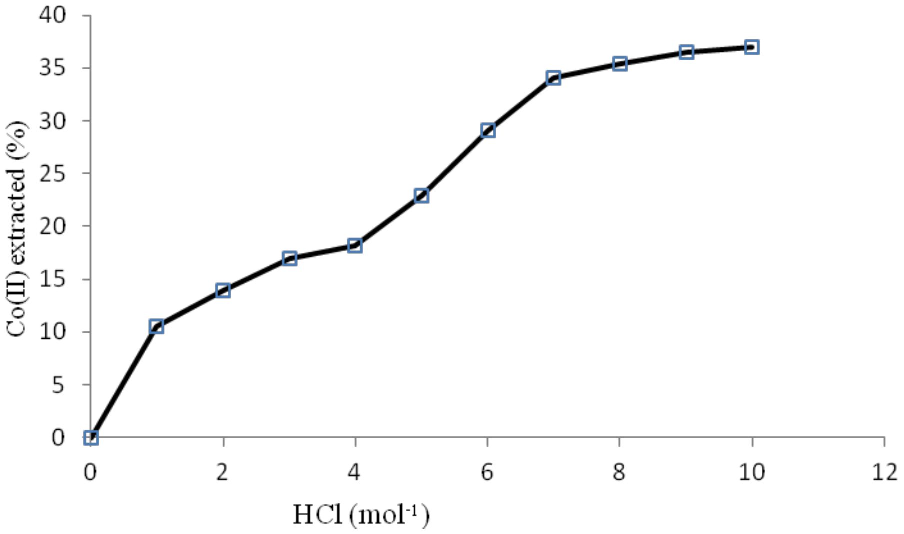

Figure 4.4: Influence of the concentration of HCl on the percentage of Co(II) extracted into a 40% (w/w) Aliquat 336/PVC membrane from a 100 mL solution containing 100 ppm Co(II).

The membrane reached saturation extraction, that is, no further Co(II) could be extracted on to the membrane, because all the cobalt(II) had 'complexed' with the available Aliquat 336 after 90 minutes. The membrane was initially clear and transparent and after the extraction became bright blue which suggested the presence of the $HCoCl_4^-$ or $CoCl_4^{2-}$ anion, on the Aliquat 336 matrix [137]. Using the methods for the identification of this complex that will be discussed later in this Chapter, it was verified that one of the complexes on the membrane was $CoCl_4^{2-}$.

4.2.1.4 Influence of hydrochloric acid concentration on the membrane extraction studies of nickel(II), iron(II) and iron(III)

Similar studies to those carried out for cobalt(II) were done for the extraction of nickel(II), iron(II) and iron(III) from varying concentrations of hydrochloric acid using the 40% (w/w) Aliquat 336/ PVC membrane and curves of a very similar shape to that of cobalt(II) were obtained at concentrations of 1M for nickel(II) and 3M for the iron(II) and iron(III). This was observed to be the optimum concentration of chloride ions for the extraction data. The extraction curves that were obtained are shown in Figure 4.5 below.

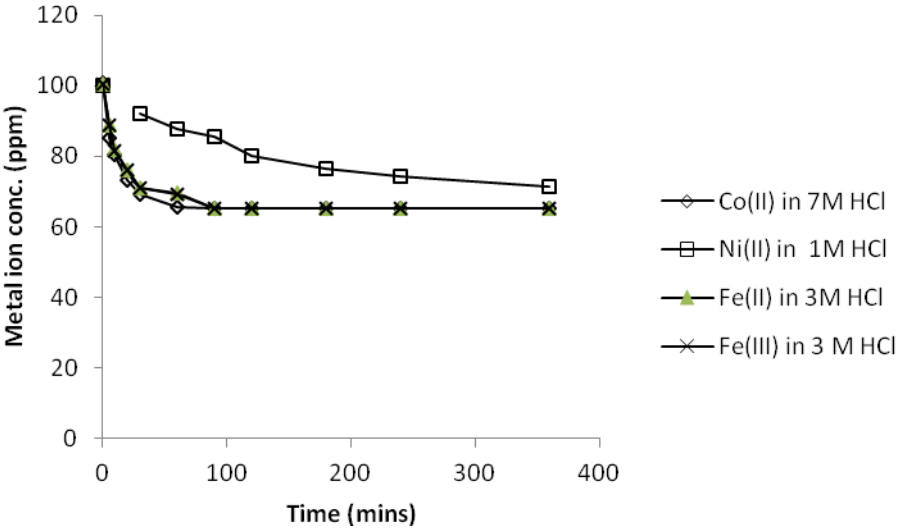

Figure 4.5 Concentration of metal ion extracted in varying HCl using 40% (w/w) Aliquat 336/PVC membrane versus time

The membranes were kept after the extraction for analysis by UV spectroscopy, which was used to confirm the identity of the extracted species. The membranes were observed to be bright blue in colour for Co(II), green for Ni(II) and yellow for Fe(II) and Fe(III).

The extractant that was used was a high molecular weight quaternary ammonium salt, Aliquat 336, which has a general formula of $R'R''R'''CH_3N^+ Cl^-$ where R represents the various lengths of the alkyl group (C_8 to C_{12}). The extraction that occurs is by ion-pair formation which was discussed in more detail in Chapter Two. A feature of quaternary ammonium compounds is their ionic character and high molecular weight salts are only sparingly soluble in water and are assumed to behave as strong electrolytes because the cation acts as a strong base [138]. In contrast primary, secondary and tertiary amines require protonation before they can act as an anion exchanger. The extraction of metal complexes occurs by anion exchange reactions and the controlling factor is the concentration of the anion that is attached to the extractant and the dominant anionic species in the aqueous solution.

As a result of these initial extractions it has been shown that the concentration of chloride ions plays an important role in the efficiency of the extraction of these metal ions. Each metal can be extracted at a specific concentration. Co(II) can be most effectively extracted from 7.0M HCl, Ni(II) from 1.0M HCl and both Fe(II) and Fe(III) from 3.0M HCl using the 40% (w/w) Aliquat 336/PVC membrane. The percentage extraction for each if the metals studied is shown in Figure 4.6 below.

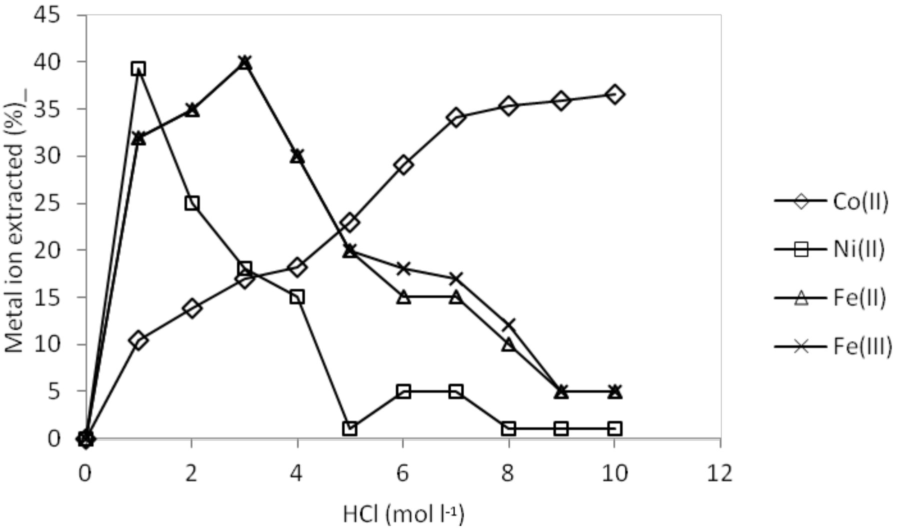

Figure 4.6 Influence of concentration of HCl on the percentage of metal ion extracted into a 40% (w/w) Aliquat 336/PVC membrane from 100mL solution of the metal ion containing 100ppm of the metal ion

4.2.1.5 The influence of metal ion concentration on extraction efficiency

Varying concentrations of Co(II) were used to study the effect of Co(II) concentration on the efficiency of extraction into the membrane in order to see of there was any effect arising from this. Solutions containing 60, 100, 152, 175, 211 and 336 ppm Co(II) in 7M HCl were prepared and using the 40%(w/w) Aliquat 336/PVC membrane the extraction curves were obtained and are shown in Figure 4.7. These showed a very similar trend to the initial extraction curves that were shown, and the only limiting factor appears to be the amount of Aliquat 336 available for complex formation in the matrix of the membrane.

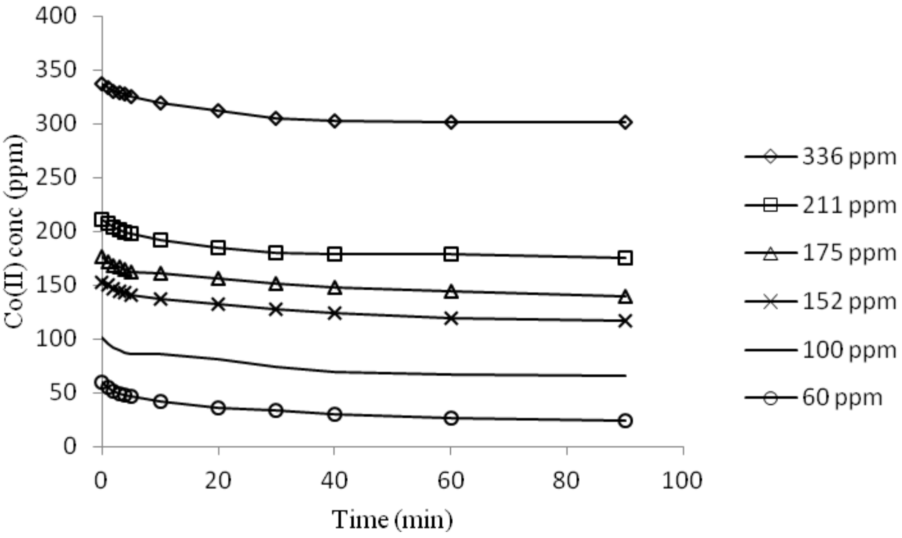

Figure 4.7 Varying concentrations of Co(II) extracted in 7M HCl using the 40% (w.w) Aliquat 336/PVC membrane.

The extraction curve for each of the initial concentrations shows a uniform trend. The results for the back extraction and the chemical analysis is discussed and shown in Table 1 in the following section.

Different concentrations of Ni(II) were also studied to examine the effect on the efficiency of extraction on to the membrane. Solutions containing 300, 200, 150,100 and 50 ppm Ni(II) in 1.0M HCl were prepared and using the 40% (w/w) Aliquat 336/PVC membrane, the extraction curves were obtained, showing a uniform trend for the extraction of nickel(II), that would suggest that the change in concentrations of the metal ion had no effect on the efficiency of the extraction as shown in Figure 4.8.

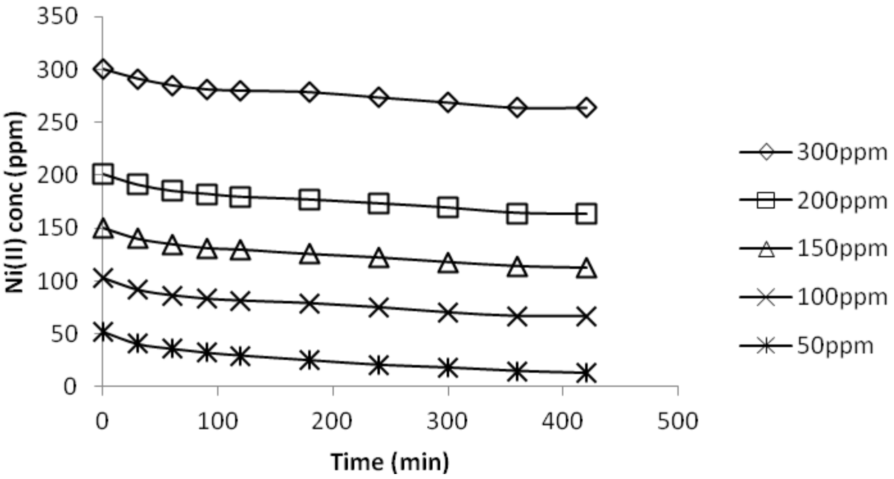

Figure 4.8 Varying concentrations of Ni(II) extracted in 1M HCl using the 40% (w.w) Aliquat 336/PVC membrane.

Varying concentrations of Fe(III) were also studied to determine if there was any effect on the efficiency of extraction on to the membrane. Solutions containing 212, 102, and 66 ppm in 3.0M HCl were prepared and using the 40% (w/w) Aliquat 336/PVC membrane, the extraction curves in Figure 4.9 show a uniform trend. It can be seen that by varying the concentrations of the metal ion of interest there is no difference in the efficiency of extraction.

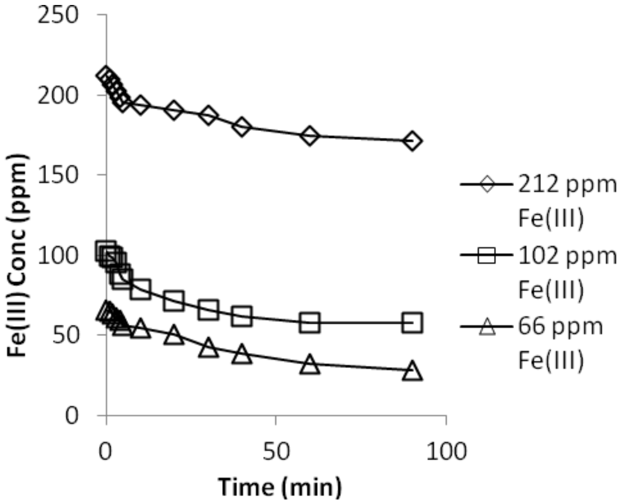

Figure 4.9 Varying concentrations of Fe(III) extracted in 3M HCl using the 40% (w.w) Aliquat 336/PVC membrane.

4.2.1.6 Back extraction studies

Back extraction (“stripping”) experiments involving different concentrations of HCl (0 – 5.0 M) in the back extraction solution revealed that the degree of back extraction increased with decreasing concentration of HCl. It was established that deionised water was capable of rapid and quantitative back extraction of the Co(II), Ni(II), Fe(II) and Fe(III) from the Aliquat 336/PVC membranes. This is demonstrated for Co(II) in Fig. 4.10 which shows both the extraction and back extraction curves for the 40% (w/w) Aliquat 336/PVC membrane for an initial Co(II) aqueous concentration of 100 ppm in 7.0 M HCl and deionized water as the back extraction solution. It can been seen that the total amount of Co(II) extracted is stripped into the deionized water during back extraction at a rate that mirrors the extraction cycle. It should be noted that deionized water was also the back extraction solution of choice used by Paimin and Cattrall [86] in their solvent extraction system where cobalt(II) was the metal of interest.

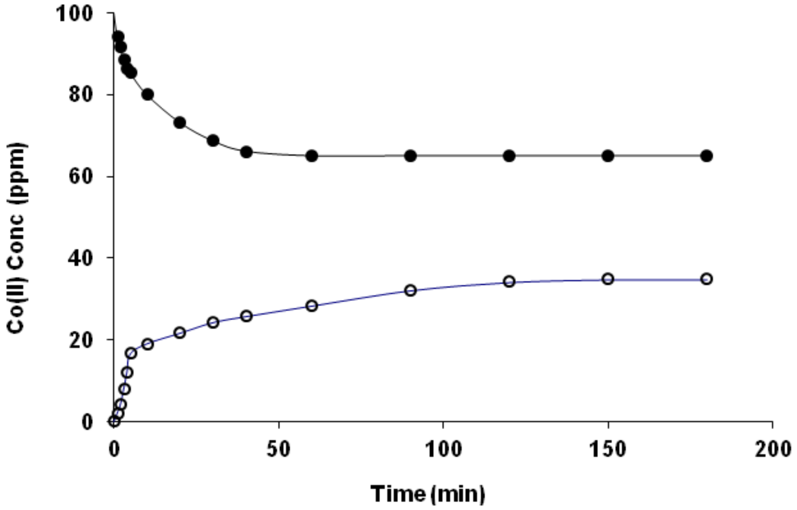

Figure 4.10 Concentration vs. time curves for the extraction and back extraction for Co(II) the 40% (w/w) Aliquat 336/PVC membrane (initial aqueous solution (●): 100 ppm Co(II) in 7M HCl; back extraction solution (○): deionized water).

Concentrations of Co(II), Ni(II), Fe(II) and Fe(III) in the feed and stripping solutions were determined by atomic absorption spectrometry, and the concentration of the H^+ ion in the stripping solution was measured potentiometrically. The determination of the chloride ion concentration in the stripping solution was based on direct precipitation titration with a standard 0.010 M solution of $AgNO_3$ using fluorescein indicator [135].

In order to establish the species that was extracted in to the membrane matrix a chemical analysis of the stripping solutions that had been used in the back extraction of Co(II) from 60, 100, 152, 175, 211, and 336 ppm solutions in 7.0 M HCl was carried out. This was done in order to identify the ion-pairs that are formed with the Aliquat 336 in the membrane matrix. The analysis revealed that the ratio between the molar concentrations of H^+, Co^{2+} and Cl^-. This would suggest that the extracted species was $[HCoCl_4]^-$. The results of the stripping solution analysis are shown in Table 4.1.

Table 4.1. Mole ratios of H/Co/Cl in the stripping solution after the back extraction of Co(II) using varying concentrations with 40% (w/w) Aliquat 336/PVC membrane in a single vessel.

initial conc. of Co(II) in 7M HCl (ppm)	Conc./100mL H^+ x10^{-4} (ppm)	Conc./100mL Co(II) x10^{-4} (ppm)	Conc./100mL Cl^- x10^{-4} (ppm)	Mole ratio H^+	Mole ratio Co(II)	Mole ratio Cl^-
336	3.57	3.530	10.70	1.0±0.03	1.00±0.05	3.03±0.05
211	3.57	3.535	10.71	1.01±0.03	1.00±0.05	3.03±0.05
175	3.57	3.535	10.70	1.01±0.03	1.00±0.05	3.03±0.05
152	3.57	3.535	10.71	1.01±0.03	1.00±0.05	3.03±0.05
100	3.57	3.535	10.71	1.01±0.03	1.00±0.05	3.03±0.05
60	3.57	3.53	10.71	1.01±0.03	1.00±0.05	3.03±0.05

Depending on the ion pair formed the back extraction will take place according to one of the following stoichiometric equations:

$A^+ [CoCl_3]^- \Leftrightarrow CoCl_2 + ACl$ Eq.1

$A_2 [CoCl_4]^{2-} \Leftrightarrow CoCl_2 + 2ACl$ Eq.2

If only the two pairs mentioned above (i.e, $A^+ [CoCl_3]^-$ and $A_2 [CoCl_4]^{2-}$) are responsible for the extraction of Co(II) into Aliquat 336/PVC membranes, the [Co(II): Cl^-] ratio in the back extraction should be 1:2 [64], However the experimentally measured ratio was found to be 1:3.

This result is similar to that obtained by Paimin and Cattrall [86] in their solvent extraction studies where they determined that the ratio between the molar concentrations of H^+, Co(II) and Cl^- in the back extraction solution was the same as found above. Paimin and Cattrall [86] proposed that the extracted Co(II) species on the membrane was $[HCoCl_4]^-$ and that the extracted complex had the formula $A^+[HCoCl_4]^-$.

The back extraction would be described by

$A^+ [HCoCl_3] \Leftrightarrow CoCl_2 + ACl + HCl$ Eq. 3

Table 4.2. Mole ratios of H/Ni/Cl in the stripping solution after the back extraction of Ni(II) using varying concentration with 40% (w/w) Aliquat 336/PVC membrane in a single vessel.

initial conc. of Ni(II) in 1M HCl (ppm.)	Conc./100mL H^+ x10^{-4} (ppm.)	Conc./100mL Ni(II) x10^{-4} (ppm.)	Conc./100mL Cl^- x10^{-4} (ppm.)	Mole ratio H^+	Mole ratio Ni(II)	Mole ratio Cl^-
100	0	3.530	10.70	0.0±0.005	1.00±0.05	3.01±0.05

Back extraction experiments involving varying concentrations of HCl (0 – 1.0 M) in the back extraction solution revealed that the degree of back extraction increased with decreasing concentration of HCl. It was established that deionised water was capable of quantitative back extraction of the Ni(II) from the Aliquat 336/PVC membranes. The stripping solution was analysed for the presence of nickel, hydrogen ion and chloride. The mole ratios are shown in Table 4.2 above, suggesting that the extracted species was $[NiCl]_4^{2-}$ and the extracted complex had the formula $A_2[NiCl_4]$ where A^+ represents the quaternary ammonium cation in the membrane of Aliquat 336.

Table 4.3. Mole ratios of H/Fe(II)/Cl in the stripping solution after the back extraction of Fe(II) using varying concentration with 40% (w/w) Aliquat 336/PVC membrane in a single vessel.

initial conc. of Fe(II) in 1M HCl (ppm)	Conc./100mL H^+ x10^{-4} (ppm)	Conc./100mL Fe(II) x10^{-4} (ppm)	Conc./100mL Cl^- x10^{-4} (ppm)	Mole ratio H^+	Mole ratio Fe(II)	Mole ratio Cl^-
100	0	3.530	7.0	0.0±0.005	1.00±0.005	2.01±0.005

Table 4.4. Mole ratios of H/Fe(III)/Cl in the stripping solution after the back extraction of Fe(III) using varying concentration with 40% (w/w) Aliquat 336/PVC membrane in a single vessel.

initial conc. of Fe(III) in 1M HCl (ppm)	Conc./100mL H^+ x10^{-4} (ppm)	Conc./100mL Fe(III) x10^{-4} (ppm)	Conc./100mL Cl^- x10^{-4} (ppm)	Mole ratio H^+	Mole ratio Fe(III)	Mole ratio Cl^-
100	0	3.530	10.70	0.0±0.005	1.00±0.005	3.01±0.005

It was also established that deionised water was capable of quantitative back extraction of the Fe(II) and Fe(III) from the Aliquat 336/PVC membranes. The stripping solution was analysed for the presence of iron, hydrogen ion and chloride ion. The chemical analysis of the stripping solution are shown in Table 4.3 and 4.4, suggesting that the extracted species for Fe(II) was $[FeCl_3]^{-1}$ and the extracted complex had the formula $A[FeCl_3]$ and the extracted species for Fe(III) was $[FeCl_4]^{-1}$ and the extracted complex had the formula $A[FeCl_4]$.

4.2.1.7 The postulation of the extracted species and mechanism of the membrane extraction from the equilibrium studies

In the studies of the extraction of gold and cadmium from Aliquat 336/PVC [23, 26, 28, 29] it was established that an anionic metal complex $AuCl_4^-$, in the case of gold , Au(III), was involved in an ion-exchange reaction with Aliquat 336 at the membrane surface to form an ion-pair which then entered the membrane. A similar mechanism can be proposed for the extraction of Co(II). Further evidence for the mechanism has also been proposed in extraction studies of Co(II) and Aliquat 336 [63, 64, 86].

The mechanism for the membrane extraction is more fully discussed where the speciation diagram and stability constants of aqueous Co(II) chlorocomplexes at different concentrations of hydrochloric acid are used to show the most likely Co(II) complex that will be formed. The formation of these complexes is thought to take place by symport transportation that was discussed in Chapter Two.

The extraction mechanism can be classified into two main categories depending on where the extraction takes place. In the case of a homogeneous mechanism, the distribution of the reagent between the organic and aqueous phases is involved. The “complexation” that occurs in this situation may be described as adduct formation, ion-exchange or chelation within the aqueous phase and is followed by the distribution of the complex at the organic phase. For a heterogeneous mechanism to occur the processes must take place at the membrane interface where there will be the diffusion of the reagent to the interface and ‘ion-pairing’ at the interface and then diffusion of the complex that is formed away from the membrane interface.

It is proposed that the metal complexes that are formed when high molecular weight quaternary ammonium salts such as Aliquat 336 are used as the extractant and the metal species to be extracted is present in aqueous acidic solutions, that the anion-exchange process occurs at the membrane interface with the feed solution, and the metal ion complex is formed.

Studies of the speciation of such complexes at various concentrations of the acidic media and information that can be obtained from the back extraction of the membrane with deionised water such as was shown in this Chapter, can be used to confirm the most likely species that will be formed. The nature of the metal ion complex can be further substantiated from information that can be obtained from UV spectral studies.

In HCl solutions, Co(II) can form four chlorocomplexes, $CoCl_n^{2-n}$ where n=1, 2, 3 4. The distribution of these complexes as a function of the concentration of HCl between 5.0 and 10.0M is shown in Figure 4.11.

The stability constants of the Co(II) chlorocomplexes (Eq. (1)) at 25°C and concentrations of HCl higher than 5.0 M, used in the calculations of the fraction of each chloride complex, are: log K_1= -1.05, log K_2= -2.69, log K_3= -1.54, and log K_4= -1.34. These values were experimentally determined by Bjerrum *et al.* [139]

$$K_n = \frac{[CoCl_n^{2-n}]}{[CoCl_{n-1}^{3-n}]\, a_{Cl^-}} \quad (n=1,2,3,4) \qquad \text{Eq.(4)}$$

The activity of the chloride ion in Eq. (1) was calculated by the one parameter activity function (Eq. (2)) introduced by the same researchers [139].

$$a_{Cl^-} = [Cl^-]10^{([Cl^-]-0.5)} \quad \text{Eq.(5)}$$

For the selective extraction of the metal species Co(II), the concentration of the anion such as chloride has been shown to be the key factor for the metal complex formation with the Aliquat 336. It can be postulated that the reason for this may be the types of complexes that are formed and previous studies by various researchers show that at various concentrations of the anion a speciation diagram can be used to support the types of complexes that are preferentially formed at a range of concentrations.

Figure 4.11 shows that the concentrations of the neutral and two negatively charged Co(II) chlorocomplexes that are capable of forming ion-pairs with the Aliquat 336 cation at the membrane/solution interface and that start to increase at HCl concentrations higher than 5.0 M. From the speciation diagram of Co(II) it can be seen that at low HCl acid concentrations the cobalt chloride does not form a complex with the chloride ions, but they remain as neutral, that is $CoCl_2(H_2O)_6$, Co^{2+}, Cl^- ions in solution

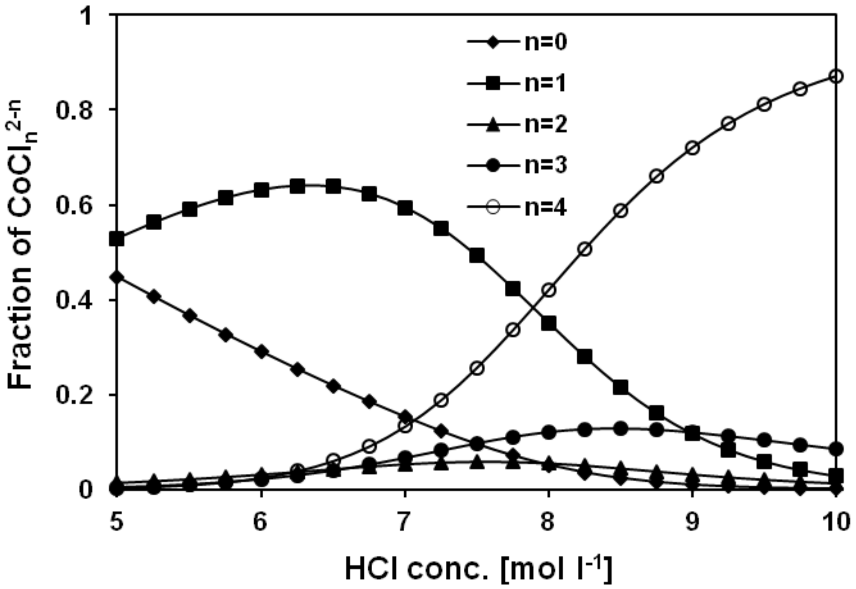

Figure 4.11 Speciation diagram for aqueous Co(II) chlorocomplexes at different concentrations of hydrochloric acid. [139]

This finding agrees with the experimental results from the extractions done that show improved extraction of Co(II) at higher concentrations of HCl (Table 4.5).

Table 4.5 Influence of the hydrochloric acid concentration on the percentage of Co(II) extracted into a 40% (w/w) Aliquat 336/PVC solid absorbent membrane from a solution containing 100 ppm Co(II).

HCl conc. [M]	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Co(II) extracted (%)	10.5	13.9	17.0	18.2	23.0	29.1	34.1	35.3	35.9	36.5

As can be seen from the speciation diagram, the metal to be extracted can only be in the anionic form of the complex (in the case of Co(II) in HCl medium, $[CoCl_3]^-$, $[CoCl_4]^{2-}$, $[HCoCl_4]^-$, Co^{2+}, $[CoCl]^+$, $[CoCl_2]$, $[HCoCl_3]$ are the species that can exist but only $[CoCl_3]^-$, $[CoCl_4]^{2-}$, $[HCoCl_4]^-$ can form ion -pairs with Aliquat 336, and thus be extracted by Aliquat 336. The formation of these metal anions depends on the formation constants of these metal complexes. The higher the formation constant, obviously the greater will be the amount of these anionic complex formed. This is also dependent on the amount of chloride available. Thus, various anionic species of the metals can be extracted at different anion concentrations. The same principle applies for Cl^-, SO_4^{2-}, NO_3^- and $C_2O_4^{2-}$ that were used in the metal extractions that are discussed later in this Chapter.

The following stoichiometric equations describe possible extraction processes involving the Co(II) chlorocomplexes mentioned above (i.e., $[CoCl_2]$, $[CoCl_3]^-$ and $[CoCl_4]^{2-}$):

$$[CoCl_2]_S + ACl_M \Leftrightarrow A^+[CoCl_3]_M^- \qquad \text{Eq.(6)}$$

$$[CoCl_3]_S^- + ACl_M \Leftrightarrow A^+[CoCl_3]_M^- + Cl_S^- \qquad \text{Eq.(7)}$$

$$[CoCl_4]_S^{2-} + 2ACl_M \Leftrightarrow A_2^+[CoCl_4]_M^{2-} + 2Cl_S^- \qquad \text{Eq. (8)}$$

where $\mathbf{A^+}$ is the Aliquat 336 cation and subscripts **S** and **M** refer to the solution and membrane phases, respectively.

It has been established that in the solvent extraction of metal chlorocomplexes with Aliquat 336 chloride, solvents with higher viscosity favor the extraction of the smaller sized ion-pair (Eq. 7). Since the viscosity of a PVC-based plasticized membrane is considerably higher compared to the organic phases used in liquid-liquid extraction, it can be expected that the trichlorocobaltate(II) complex will be extracted preferentially into Aliquat 336 chloride /PVC membranes (Eqs.(6) and (7)). than the tetrachlorocobaltate(II) complex (Eq.(8)). In addition to the viscosity factor, the extraction of $[\mathrm{CoCl_4}]^{2-}$ will be inhibited because the corresponding extraction reaction (Eq.(5)) requires the participation of two adjacent interfacial Aliquat 336 chloride molecules instead of one as in Eqs. (6) and (7).

Depending on the ion-pair formed, back extraction will take place according to one of the following stoichiometric equations:

$$\mathrm{A^+[CoCl_3]^-_M \Leftrightarrow ACl_M + [CoCl_2]_S} \qquad \text{Eq.(9)}$$

$$\mathrm{A^+_2[CoCl_4]^{2-}_M \Leftrightarrow 2ACl_M + [CoCl_2]_S} \qquad \text{Eq.(10}$$

If only the two ion-pairs mentioned above (i.e., $\mathrm{A^+[CoCl_3]^-}$ and $\mathrm{A^+_2[CoCl_4]^{2-}}$) are responsible for the extraction of Co(II) into Aliquat 336/PVC membranes, the [Co(II)]:[Cl$^-$] ratio in the back extraction solution should be 1:2. However, the experimentally measured [Co(II)]:[Cl$^-$] ratio was found to be 1:3. This result supports the conclusion that Paimin and Cattrall [86] reached in their solvent extraction studies that Co(II) is extracted into the membrane as the $\mathrm{A^+[HCoCl_4]^-}$ ion-pair which upon back extraction (Eq. (11)) will release H$^+$, Co(II) and Cl$^-$ ions in the ratio

[H$^+$]:[Co(II)]:[Cl$^-$] = 1:1:3 in the stripping solution.

$$\mathrm{A^+[HCoCl_4]^-{}_M \Leftrightarrow ACl_M + [CoCl_2]_S + H^+_S + Cl^-_S} \qquad \text{Eq. (11)}$$

The extraction process in this case can be described by Eqs. (12) and (13):

$$\mathrm{[CoCl_4]^{2-}_S + H^+ + ACl_M \Leftrightarrow A^+[HCoCl_4]^-{}_M + Cl^-_S} \qquad \text{Eq. (12)}$$

$$[\mathrm{CoCl_3}]^-_S + \mathrm{H}^+ + \mathrm{ACl}_M \Leftrightarrow \mathrm{A}^+[\mathrm{HCoCl_4}]^-{}_M \qquad \text{Eq. (13)}$$

It is also possible that the formation of $\mathrm{A}^+[\mathrm{HCoCl_4}]^-$ at the membrane/solution interface may involve participation of the aqueous complexes $[\mathrm{HCoCl_4}]^-$ and $[\mathrm{HCoCl_3}]$ (Eqs. (14) and (15)).

$$[\mathrm{HCoCl_4}]^-_S + \mathrm{ACl}_M \Leftrightarrow \mathrm{A}^+[\mathrm{HCoCl_4}]^-{}_M + \mathrm{Cl}^-_S \qquad \text{Eq. (14)}$$

$$[\mathrm{HCoCl_3}]_S + \mathrm{ACl}_M \Leftrightarrow \mathrm{A}^+[\mathrm{HCoCl_4}]^-{}_M \qquad \text{Eq. (15)}$$

Further support is provided by the work of Belousov and Ivanov [140], who confirmed the presence of complex acids of chlorocobaltate(II) species in concentrated HCl by determining the dissociation constants of the complex acids $[\mathrm{HCoCl_3}]$ (K_d=6.60x10^2) and $[\mathrm{H_2CoCl_4}]$ ($K_{d,1}$=6.85x10^3, $K_{d,2}$=3.60x10^1). It can be calculated that the concentrations of both $[\mathrm{HCoCl_4}]^-$ and $[\mathrm{HCoCl_3}]$ increase with the concentration of HCl, though their concentrations remain substantially lower (i.e., more than an order of magnitude) than those of the corresponding proton-free chloride complexes (i.e., $[\mathrm{CoCl_3}]^-$ and $[\mathrm{CoCl_4}]^{2-}$)[64].

Further experiments to confirm the extracted species in the equilibrium studies were also carried out with LiCl, KCl, NaCl and $\mathrm{CaCl_2}$ in order to obtain a broader range of extraction results to better define the effect of the concentration of the anion involved in the extraction of cobalt(II).

The cobalt(II) was extracted from solutions of 7M LiCl with varying Aliquat336/PVC membrane compositions so as to select the optimum conditions for extraction, which was determined to take place with the 40% (w/w) Aliquat 336/PVC membrane . In order to compare the extraction of HCl and LiCl, extraction studies were carried out for 100ppm Co(II) feed solution made up from various concentrations of LiCl. Solutions containing the cobalt(II) in 7.0M, 6.0M. 5.0M, 3.0M and 1.0M LiCl were used for the extraction process and these results are illustrated in Figure 4.12. The initially clear membrane was found to be bright blue when the Co(II) was extracted again suggesting the presence of the $CoCl_4^{2-}$ anion.

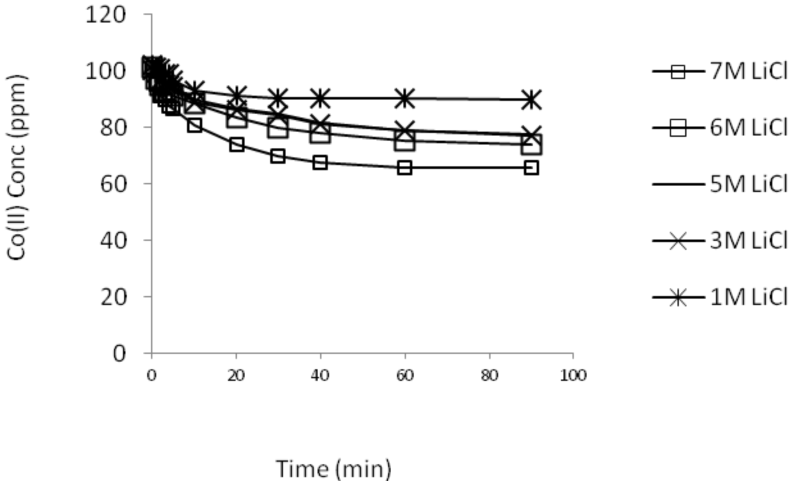

Figure 4.12. Concentration vs. time curves for the extraction of Co(II) concentration vs. time of contact (initial concentration of aqueous Co(II) in varying concentrations of LiCl solution (100ppm.) for the 40% (w/w)Aliquat 336/PVC membrane.

The results for the extraction of Co(II) in both HCl and LiCl are very similar, suggesting that a similar mechanism of extraction was involved. Extraction studies of LiCl at concentrations ranging from 7.0M to 1.0M LiCl were also carried out to determine whether lithium could be extracted into the membrane. It was found that no lithium was extracted either into or onto the membrane. This was identified by atomic absorption spectrometry of solution samples as previously described for the extraction process. The possible explanation for this is that lithium does not readily form chloro-complexes. However, the opposite was proposed by Kagaya *et al*. [136] who suggested that the ion pairs formed with the Aliquat 336 cation, may possibly be $R_3MeN^+.LiCl_2$. Further experiments were carried out in order to make the studies more comprehensive and complete and to further confirm the composition of the extracted species, solutions of 5.0M, 3.0M and 1.0M KCl and 5.0M, 3.0M and 1.0M NaCl using 40%(w/w) Aliquat 336/PVC membranes were also used for the extraction of cobalt(II).

The extraction studies of KCl and NaCl at concentrations ranging from 1.0M to 5.0M KCl were also carried out in order to determine whether potassium or sodium could be extracted into the membrane. It was found that none was extracted either into or onto the membrane as potassium and sodium do not readily form chloro-complexes. The successful use of sodium chloride for the extraction process was a valuable discovery, in that it is a non- toxic chemical compared with both potassium chloride and lithium chloride which are carcinogenic, and hydrochloric acid which is corrosive and hazardous. Sodium chloride is very cost efficient and an environmentally safe alternative to species that are currently being used. The initially clear membrane was found to be bright blue when the Co(II) was extracted again suggesting the presence of the $CoCl_4^{2-}$ anion. (A section of this membrane was also examined using UV spectroscopy that confirmed the presence of $CoCl_4^{2-}$). The results for extraction of Co(II) in both KCl and NaCl also show marked similarity to each other as well as to that in 7.0M HCl and 7.0M LiCl.

As was discussed earlier, due to the solubility of KCl and NaCl, solutions with concentrations of more than 5.0M are not feasible, however, the use of these as extraction media is of great interest as they are not only extremely cost effective, but in the case of sodium chloride, chemically safe for prolonged or continuous use.

Equilibrium studies [40, 41, 79] were carried out for the extraction of cobalt(II) from the 7M LiCl, 5M KCl and 5M NaCl. The cobalt (II), lithium, potassium and sodium analyses were done using atomic absorption spectrometry and the chloride ion determined titrimetrically as previously described [63, 64, 86, 135]. The results were used to determine the mole ratio of Li/Co/Cl, K/Co/Cl and Na/Co/Cl respectively, and found to be 0:00: 1.00 ± 0.005: 3.00 ± 0.005 in each case for the extracted solution, which would indicate that the complex in the membrane matrix was likely to be cobalt tetrachloride.

The results above related to the extraction of Co(II) with chloride media with monovalent metal ions. More evidence for confirmation of the proposed mechanism is provided by carrying out similar extraction studies using a divalent metal ion that cannot form chloride complexes, in this case calcium(II). The results are very similar and it should be noted that the solubility of calcium chloride prevents concentrations higher than

3.5M being obtained. Further equilibrium studies were done for the extraction of cobalt(II) in 3.5M $CaCl_2$. The analysis of calcium was done using atomic absorption spectrometry and the chloride ion determined titrimetrically [135] and the results used to determine the mole ratio of Ca/Co/Cl respectively. The mole ratio was found to be 0:0:1.01:2.99 $\pm$0.005. The initially clear membrane was found to be bright blue when the Co(II) was extracted again suggesting the presence of the $CoCl_4^{2-}$ anion in the membrane matrix. This would be expected as calcium chloride is unable to form any chloride complexes and this was confirmed by trying to extract Ca(II) using the PVC/ Aliquat membrane system previously described. The results of this investigation showed no extraction of the calcium into the membrane.

Close agreement between the extraction of Co(II) in all of the chloride media used was observed. In all the media the predominant species of the Co(II) extracted has been shown to be $[CoCl_4]^{2-}$, except in HCl and in this medium, $[HCoCl_4]^-$ was the species being extracted by Aliquat 336. This is substantiated by the work carried out by determining the mole ratio of the Co(II) to chloride present in the back extraction studies.

Further evidence of the presence of the cobalt tetrachloride ion was also confirmed using UV visible spectroscopy [139]. Transition metals commonly exhibit absorption bands in the UV /visible region of the spectra. These often result from the energy differences in the *d*-electron states arising from the electron interactions of coordinated donor atoms, and can provide a useful tool for the identification of the complexes that are formed. These complexes can be identified by their unique absorbance peaks at specific wavelengths in the UV/Visible spectrum. The spectra were obtained from the membranes that were used to extract 100ppm Co(II) in 7M HCl and 100ppm Ni(II) in 1M HCl with a clear membrane that had not been used in the extraction work as a standard. Spectra for a range of samples are shown in Figures 4.13 and 4.14.

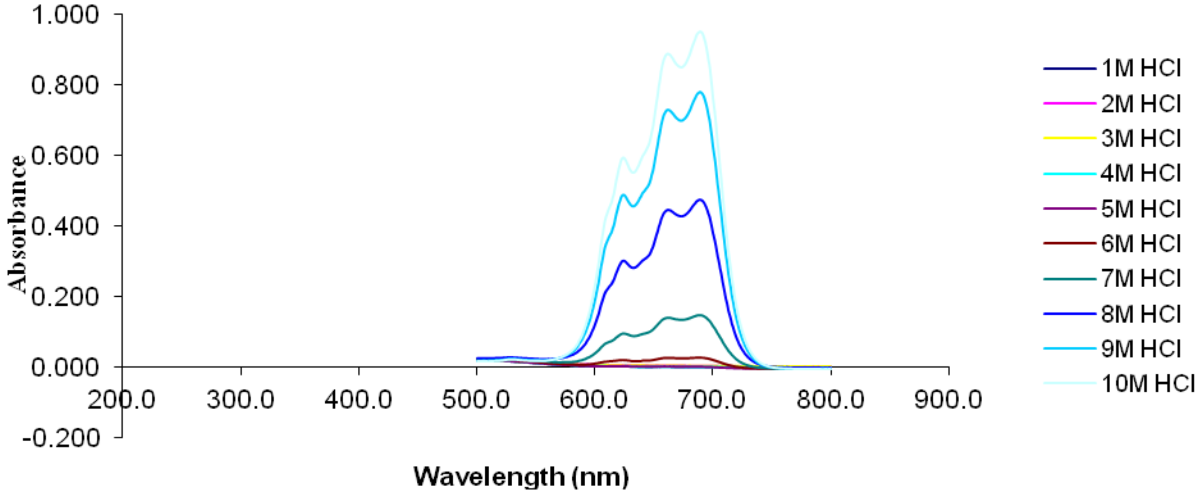

Figure 4.13 UV/Visible spectra obtained for solutions of 100ppm.of cobalt chloride in concentrations of HCl ranging from 1.0M – 10.0M.

In Figure 4.13 the UV/Visible spectra for cobalt chloride solutions prepared in various hydrochloric acid concentrations is shown. The main peaks of interest can be seen at wavelengths of 693 nm, 668 nm and 635 nm, which is consistent with the presence of the cobalt tetrachloride complex $CoCl_4^-$, which was confirmed from the work carried out by Gill and Nyholm [137].

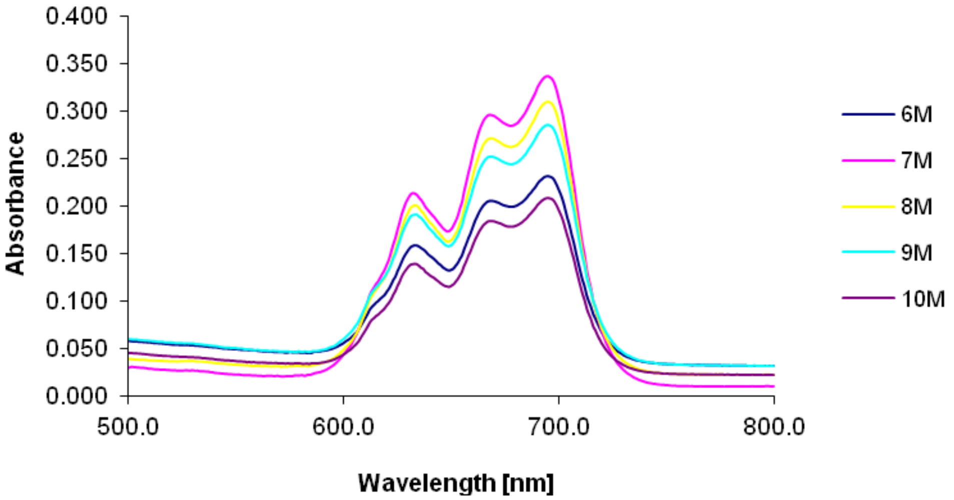

Figure 4.14 UV/Visible spectra obtained for Aliquat 336/PVC membranes obtained for the extraction of 100ppm. cobalt chloride in varying concentrations of HCl.

In Figure 4.14 the main peaks are seen at wavelengths of 693 nm 668 nm and 635 nm for 40% (w/w) Aliquat 336/PVC membranes that had been used in the extraction of 100ppm Co(II) in solutions that had concentrations of 10.0M, 9.0M, 8.0M, 7.0M and 6.0M hydrochloric acid. The peaks that were seen are consistent with the presence of the cobalt tetrachloride complex $CoCl_4^{-2}$.

UV/Visible spectra were obtained from membranes that had been used for the extraction of 100ppm cobalt(II) in 7.0M hydrochloric acid, 7.0M lithium chloride, 5.0M potassium chloride, 3.5M calcium chloride. These were selected because of the results of the membrane extraction studies that were presented in this Chapter, where the extracted species is postulated to be the same for each of the membrane extraction studies.

The peaks were seen at 693 nm, 668 nm and 635 nm in each spectrum and these peaks confirm the presence of the cobalt tetrachloride ion in the membrane. The confirmation of the complex was be used to explain and justify the mechanism of the extraction process and is further supported by the studies of Bjerrum *et al.* [139].

The extraction of Co(II) was found to be quite rapid and this was quite possibly due the high concentration of the chloride anions. It is thought to be due to an increase in reaction rates and the preferential tetrahedral structure of the cobalt tetrachloride ion that was bound in the membrane[1].

A similar mechanism can be proposed for the membrane extraction of nickel(II).
There are two anionic chlorocomplexes $MHCl_4^-$ and MCl_4^- which can interact with Aliquat 336 and these are shown in the following equations:

$$ACl_m + [NiHCl_4]^-_a \Leftrightarrow A[NiHCl_4]^-_m + Cl_a^- \qquad \text{Eq. (16)}$$

$$2ACl_m + [NiCl_4]^{2-}_a \Leftrightarrow A_2[NiCl_4]_m + 2Cl_a^- \qquad \text{Eq. (17)}$$

where M is the nickel metal and ACl is the Aliquat 336 chloride and the subscripts ‘m’ and ‘a’ refer to the membrane and aqueous phase respectively.

Further evidence for this is provided by the kinetic study of nickel(II) extraction from chloride solutions using dodecylsalicylicaldoxime [87, 88] which showed a similar interfacial mechanism between the nickel and extractant ligand.

The proposed mechanism of extraction is consistent with that described by Buch *et al.* in the extraction and back extraction of nickel using the hydroxime (2-ethylhexanal oxime) EHO as extractant [90, 91]. Nickel is strongly solvated by water molecules in aqueous solution and any chemical compound able to eliminate water molecules out of its solvation shell, such chloride ions will favour its extraction by increasing the hydrophobic factor [90, 91].

Further studies to confirm the mechanism were also carried out with LiCl, KCl, NaCl and $CaCl_2$ in order to obtain broader range of extraction results to better define the mechanism involved in the extraction of nickel(II), and which will indicate the effect of the chloride ion concentration. Solutions containing the nickel(II) in varying concentrations of LiCl, KCl, NaCl and $CaCl_2$ were used for the extraction process and the optimum extraction for nickel was shown to occur at a concentration of 1.0M for each the chloride media. Figure 4.15 below shows the comparative extraction of Ni(II) in all of the chloride media studied.

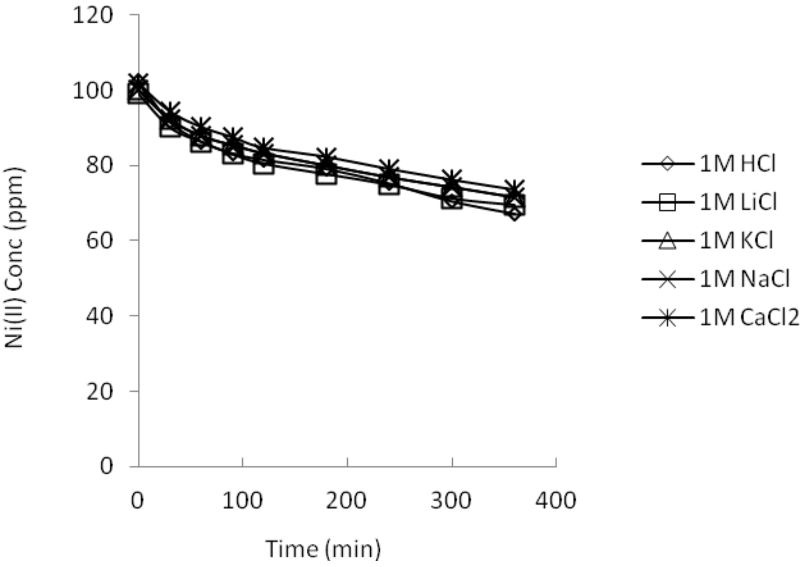

Figure 4.15 Concentration vs. time curves for the comparison of the extraction of 100ppm Ni(II) () in 1.0M, HCl, LiCl, KCl, NaCl and $CaCl_2$ solutions using 40% (w/w) Aliquat 336/PVC membrane

It can be seen from Figure 4.15 that the extraction curves are markedly similar and this implies that the mechanism of extraction is most likely to be similar in all environments studied.

Chemical analyses were done for the back extraction or stripping for each solution and in the cases of lithium chloride, potassium chloride, sodium chloride and calcium chloride and the mole ratios of metal ion, chloride ion and hydrogen ion were determined as previously described [135] and these were found to be 1.00±0.005: 3.00±0.005: 0.00 thus suggesting the presence of $NiCl_4^{2-}$ as the most likely species in the membrane matrix.

Speciation diagrams for nickel in chloride solutions were studied from a paper by Ji and Cooper [142]. The speciation diagrams that were shown were in the range of pH from 0 to 14, but there was no definitive extraction of the nickel tetrachloride species, which would have been expected from the data that was presented [142].

Nickel was able to be preferentially extracted into the Aliquat 336 /PVC membrane using a variety of chloride media which included hydrochloric acid, lithium chloride, potassium chloride, sodium chloride and calcium chloride. The extraction of nickel with chloride media showed a similar trend for each of the mediums that were used. The optimum extractability occurred at concentrations of 1.0M in each case. The mechanism for the extraction was proposed which showed good agreement with the mechanism proposed by Buch *et al*. [90, 91].

The time taken for the maximum extraction to occur was a lot longer that that for cobalt(II) and this could have been due to the fact that the concentration of the chloride anion is much lower and hence the reaction rate is lower. Another possible explanation is that the stereochemistry of the nickel tetrachloro complex is square planar rather than tetrahedral and the presence of aqua ions attached to the nickel would make it a bulkier complex that was attached to the membrane [1, 137].

UV/Visible spectra were obtained for the nickel complex that was formed after the extraction of 100ppm nickel(II) chloride in 1.0M hydrochloric acid and is shown below in Figure 4.16.

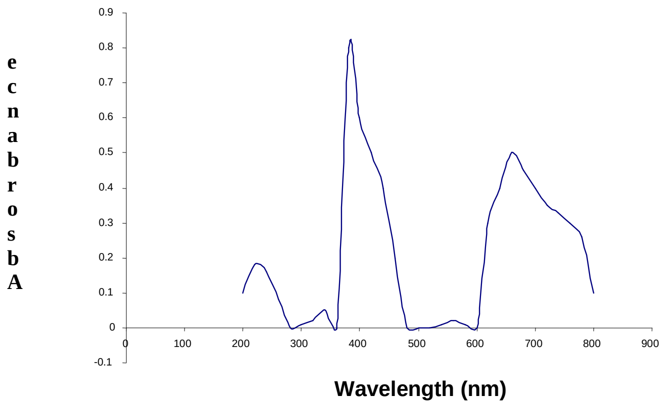

Figure 4.16 UV/Visible spectra of Aliquat 336/PVC membrane obtained after the extraction of Ni(II) in 1.0M HCl.

The main peaks are seen at wavelengths of between 700 and 660 nm. and 395 nm. and these peaks are in agreement with the literature values that were determined by Ballhausen *et al.* [141]. The bands at 700nm and 660nm denote the presence of

$NiCl_4^{-2-}$and the band at 395 nm denotes the presence of $Ni(H_2O)_6^{2+}$. The presence of the nickel tetrachloro-complex is in agreement with that which was postulated in the back extraction studies.

The extracted species in the equilibrium study can also be postulated for the membrane extraction of Fe(II) and Fe(III). The speciation diagram of Fe(II) and Fe(III) is illustrated in Figure 4.17, $FeCl_4^-$ is seen to be the most abundant at concentrations of 3M to 5M chloride. In the studies that were reported by Lui *et al*. [143], it was determined that the most abundant species at 25^{o}C was the ferric tetrachloride and the most likely stereochemistry was tetrahedral and this was supported by X-ray and fine structure spectrometry (XAFS) studies. UV spectral studies were seen to change systematically with increasing chloride concentration and the $FeCl_4^-$ predominates in solutions [143].

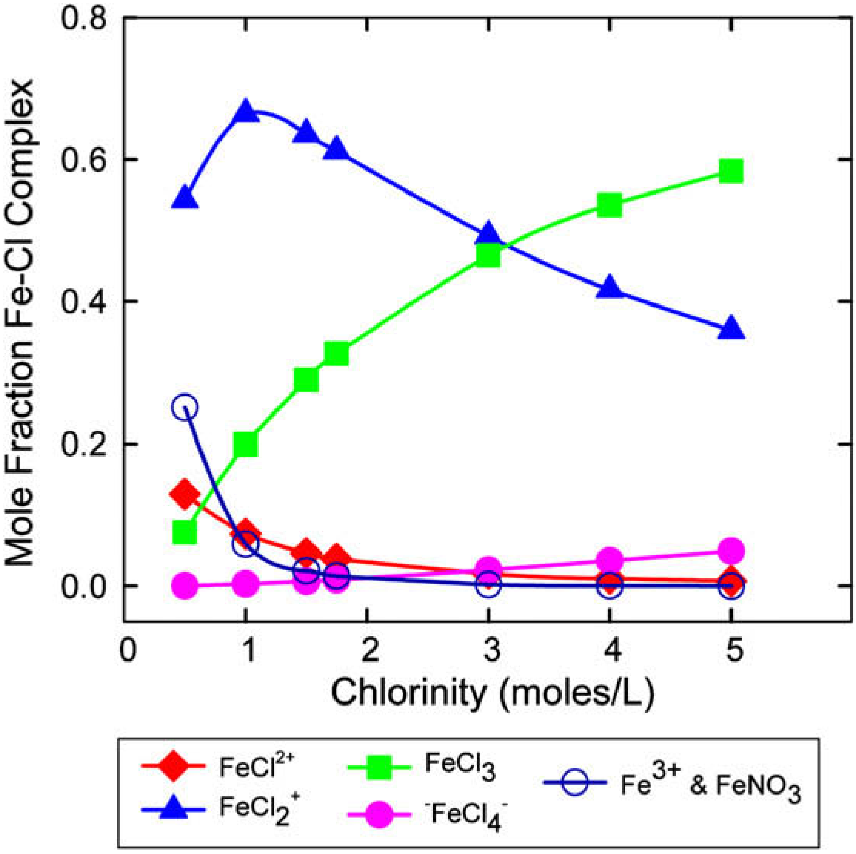

Figure 4.17 Mole fractions of the individual Fe–Cl complexes, at varying [Cl^-], relative to the total amount of iron remaining in the aqueous phase (Hill *et al*.[144]).

This work is in agreement with earlier work done by Bjerrum and Lukes who also discussed the fact that iron(II) forms weaker chloro complexes than iron(III) [145]. For the extraction of Fe(II) there are two anionic chlorocomplexes $[FeHCl_4]^-$ and $[FeCl_4]^{2-}$ which can interact with Aliquat 336 and these are shown in the following equations:

$$ACl_m + [FeHCl_4]^-_a \Leftrightarrow A[FeHCl_4]^-_m + Cl_a^- \qquad \text{Eq. (18)}$$

$$2ACl_m + [FeCl_4]^{2-}_a \Leftrightarrow A_2[FeCl_4]_m + 2Cl_a^- \qquad \text{Eq. (19)}$$

where Fe is the iron metal and ACl is the Aliquat 336 chloride and the subscripts ‘m’ and ‘a’ refer to the membrane and aqueous phase respectively.

For the extraction of Fe(III), there is one anionic chlorocomplex, $FeCl_4^-$ which can interact with Aliquat 336 and this is shown in the following equation:

$$ACl_m + [FeCl_4]^-_a \Leftrightarrow A[FeCl_4]^-_m + Cl_a^- \qquad \text{Eq. (20)}$$

Support for these proposals can be found in previous studies where the mechanism of extraction for Fe(III) in hydrochloric acid has been postulated [146]. In these studies Fe(III) was extracted in 6.0M HCl with five long chain amine chlorides in chloroform by single drop technique [146].

Again, further studies to confirm the mechanism were also done with varying concentrations of LiCl, KCl, NaCl and $CaCl_2$ in order to obtain a broader range of extraction results and to better define the mechanism involved in the extraction of iron(II) and iron(III).

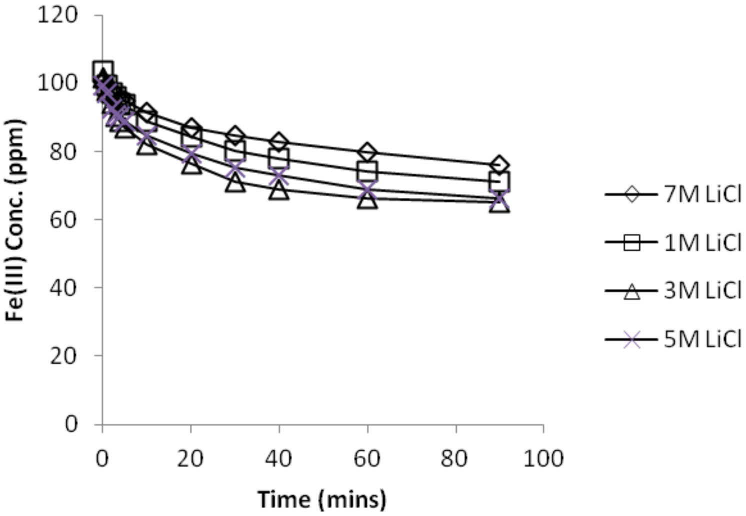

Figure 4.18 Concentration vs. time curves for the extraction of Fe(III) (initial concentration of aqueous Fe(III) in varying concentrations of LiCl solution-100ppm for the 40%(w/w) membrane. A single vessel is used for this extraction.

From Figure 4.18, the best extractability of Fe(II) and Fe(III) was seen at a concentration of 3.0M lithium chloride. Chemical analysis of the stripping solution was done as previously described and the ratios Fe(II): Li^+: Cl^- was determined to be 1.00±0.005: 0.00: 3.01± 0.005 and the ratios Fe(III) :Li^+: Cl^- was determined to be 1.00±0.005: 0.00: 3.01± 0.005. These results would suggest the presence of $[FeCl_4]^{2-}$ and $[FeCl_4]^-$ respectively being formed in the membrane matrix. Further experimental work was carried out in a similar manner using KCl, NaCl and $CaCl_2$ and the chemical analyses of the stripping solutions were done as previously described and the ratios Fe(II) :K^+: Cl^- were determined to be 1.00±0.005: 0.00: 3.01± 0.005 and for the ratios Fe(III) :K^+: Cl^- was determined to be 1.00±0.005: 0.00: 3.01± 0.005. Further chemical analyses of the stripping solution were found to show the ratios of Fe(II) :Na^+: Cl^- to be 1.00±0.005: 0.00: 3.01± 0.005 and for the ratios Fe(III) :Na^+: Cl^- to be 1.00±0.005: 0.00: 3.01± 0.005 and similarly, the chemical analysis of the stripping solutions when calcium chloride was used in the extraction process, and the ratios of Fe(II) :Ca^{2+}: Cl^- was determined to be 1.00±0.005: 0.00: 3.01± 0.005 and for the ratios Fe(III) :Ca^{2+}: Cl^- was determined to be 1.00±0.005: 0.00: 3.01± 0.005. These results would also suggest the presence of $[FeCl_4]^{2-}$ and $[FeCl_4]^-$ respectively being formed in the membrane matrix. The presence of these ions is consistent with the mechanism that has been proposed and is in good agreement with findings by Ilic *et al.* [149], who studied the transfer of Fe(III) at a free oil-water interface.

The extraction curves for the extraction of Fe(II) and Fe(III) also showed very similar characteristics and a mechanism for each species that has been proposed is in good agreement with earlier studies [149]. This is further supported by the additional extraction studies done with lithium chloride, potassium chloride, sodium chloride and calcium chloride where the optimum extraction was found to occur in 3.0M hydrochloric acid, 3.0M lithium chloride, 3.0M potassium chloride, 3.0M sodium chloride and 2.0M calcium chloride for each of the iron(II) and the iron(III) and the extraction curves showed marked similarity.

The time for the extraction was similar to that for the extraction of cobalt(II), possibly due to higher chloride anion concentration and the stereochemistry of the iron chloro- complexes being tetrahedral [1]. Each metal could be completely back extracted, that is, quantitatively stripped from the membrane in deionised water.

4.2.2 Membrane extraction studies of Co(II), Ni(II), Fe(II) and Fe(III) from sulphuric acid

Similar studies to optimize the membrane used for the extraction process were done as in the previous section for the extraction in chloride media with the 40% (w/w) Aliquat 336/PVC membrane showing the maximum efficiency. The counter-ion on the Aliquat 336 was replaced with sulphate as previously described in Chapter Three.

4.2.2.1 The influence of sulphuric acid concentration on the extraction

The effect of the concentration of the sulphuric acid was determined by extracting solutions containing 100 ppm Co(II) in varying concentrations of the sulphuric acid.
Figure 4.19 shows the extraction curves that were obtained for concentrations of 5.0M, 2.0M and 1.0M sulphuric acid.

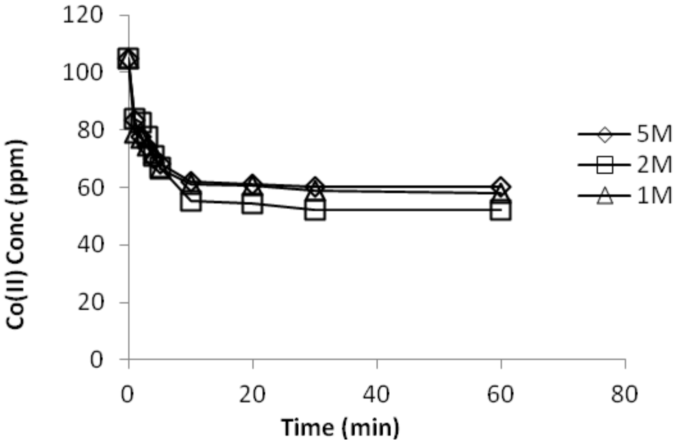

Figure 4.19 Concentration vs. time curves for the extraction of 100ppm Co(II) in 5.0M, 2.0M and 1.0M H_2SO_4 solutions using the 40%(w/w) Aliquat 336/PVC membranes.

As can be seen from the extraction curve the optimum concentration for the extraction of Co(II) is 2.0 M sulphuric acid, whilst 18 percent less Co(II) is extracted at the higher concentration of 5.0M and 28 percent less Co(II) is extracted at the lower concentration of 1.0M. The concentrations that were selected were based on information obtained from literature values.

The effect of the concentration of sulphuric acid on the extraction of Ni(II) was done using a 40%(w/w) Aliquat 336/PVC membrane. Solutions of 100ppm Ni(II) were made from nickel sulphate that was dissolved in 5.0M, 2.0M and 1.0M sulphuric acid, and although the results for extraction 5.0M and 2.0M appear very similar, a concentration of 1.0M sulphuric acid was selected as the most efficient for the extraction of nickel.

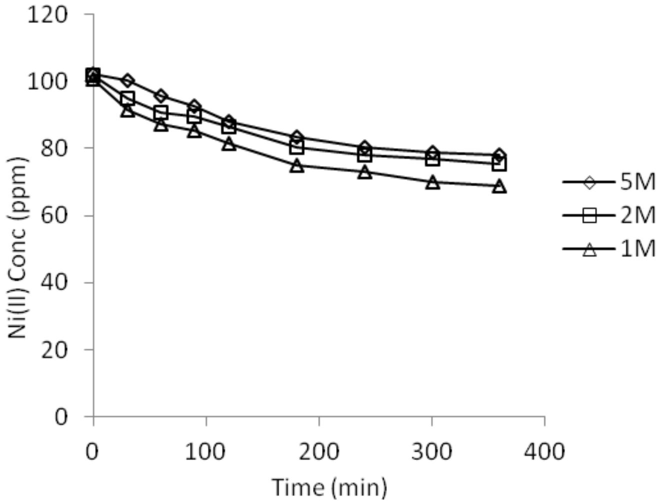

Figure 4.20 Concentration vs. time curve for the extraction of 100ppm Ni(II) in 5.0M, 2.0M and 1.0M H_2SO_4 solutions using the 40%(w/w) Aliquat 336/PVC membrane

The effect of concentration of the sulphuric acid was determined by extracting solutions of 100ppm. Fe(II) and Fe(III) in varying concentrations of sulphuric acid ranging from 1.0 – 7.0M using the membranes containing 40% (w/w) Aliquat 336/PVC for the reasons that were previously outlined.

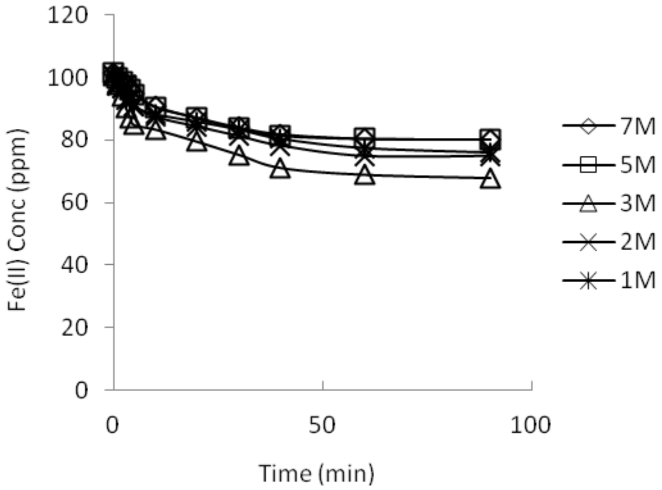

Figure 4.21 Concentration vs. time curves for the extraction of 100ppm Fe(II) in varying concentrations of sulphuric acid solution using the 40%(w/w) Aliquat 336/PVC membrane.

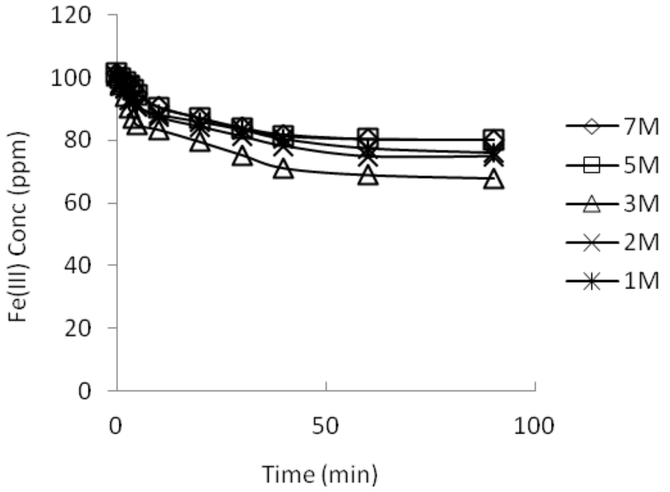

Figure 4.22 Concentration vs. time curves for the extraction of 100ppm Fe(III) in varying concentrations of sulphuric acid solution using the 40%(w/w) Aliquat 336/PVC membrane.

The extraction curves shown in Figures 4.21 and 4.22 obtained for Fe(II) and Fe(III) show similar trends and the optimum extraction of the iron occurs at a concentration of 3.0M sulphuric acid in each case.

4.2.2.2 Back extraction studies

Back extraction studies using different concentrations of sulphuric acid (1.0M, 0.5M and 0.1M) and deionised water showed that the Co(II) was completely stripped using deionised water in a similar time frame to the initial extraction time and this is shown graphically in Figure 4.23.

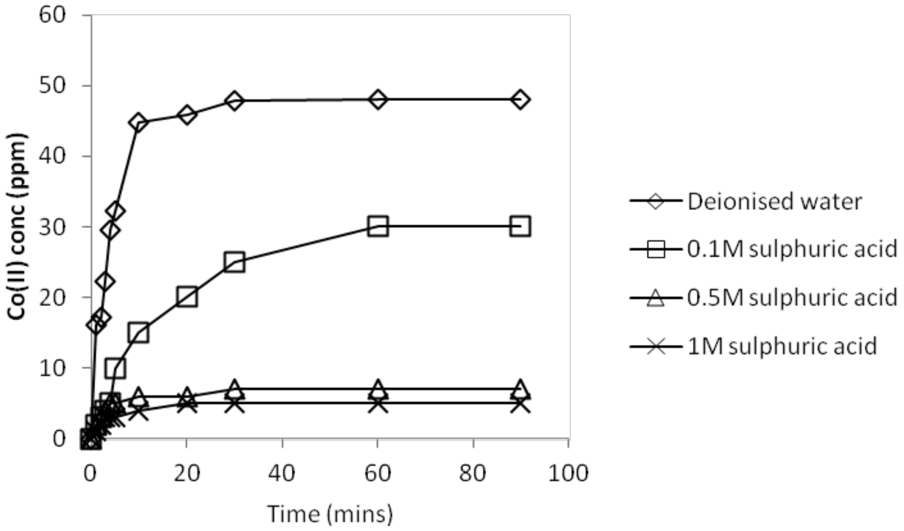

Figure 4.23 Concentration vs. time curve for the back extraction for Co(II) in deionised water, 0.1M , 0.5M and 1M sulphuric acid using 40%(w/w) Aliquat336/PVC membrane.

Equilibrium studies [43, 59, 60] were effected for the extraction of Co(II)) from 2.0M sulphuric acid. The analysis of Co(II) was carried out using atomic absorption spectrometry and the sulphate analysis was achieved by titration using a dilute solution of lead nitrate and bromophenol blue indicator [135]. The concentration of the hydrogen ion in the stripping solution was measured potentiometrically. The ratios of Co(II) :H^+: SO_4^{2-} was found to be 1.00 ± 0.05 : 0 ± 0: 00: 1.00 ± 0.03, suggesting that the extracted species was $Co(SO_4)$ and the species in the membrane matrix was $[Co(SO_4)_2]^{-2}$.

Back extraction studies using 2.0M, 1.0M sulphuric acid and deionised water showed that the nickel(II) was completely stripped from the membrane for stripping solutions of 1.0M sulphuric acid and deionised water. Figure 4.24 shows the back extraction curves for the complete stripping of Ni(II) from the membrane and there are obvious advantages in using deionised water as the stripping solution.

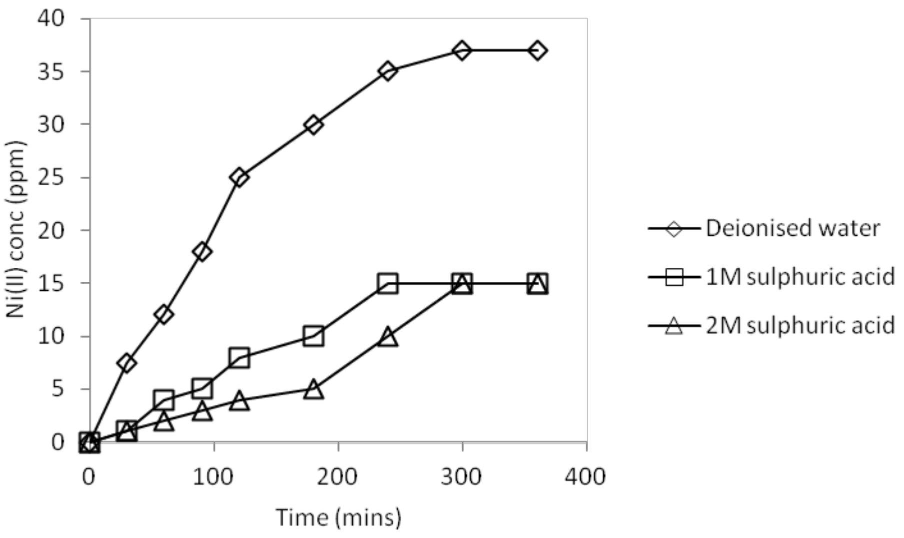

Figure 4.24. Concentration vs. time curve for the back extraction for Ni(II) in deionised water, 0.1M , 0.5M and 1M sulphuric acid using 40%(w/w) Aliquat336/PVC membrane.

The concentrations of Ni(II) in the feed and stripping solutions were determined by atomic absorption spectrometry. The concentration of the H^+ ion in the stripping solution was measured potentiometrically. The determination of the sulphate ion concentration in the stripping solution was carried out by titration using a standard solution of lead nitrate and bromophenol blue indicator [135].

The chemical analysis of the stripping solution showed that the ratio of Ni(II) , hydrogen ion and sulphate ion was 1.00 ± 0.005 :0.00± 0.005 :1.02 ± 0.005 suggesting that the extracted species was $Ni(SO_4)$ and the species in the membrane matrix was $[Ni(SO_4)_2]^{-2.}$.

Back extraction studies were also carried out for Fe(II) and Fe(III) using deioinsed water to strip the iron from the membrane, and in each case the reaction was complete. These are displayed in Figures 4.25 and 4.26. The presence of Fe(II), Fe(III), hydrogen ion and sulphate ion was measured using the same techniques as previously described. For Fe(II) the ratios of Fe^{2+}: H^+: SO_4^{2-} were found to be 1.00 ± 0.003: 0.0: 1.00 ± 005 and for Fe(III) the ratios of Fe^{3+}: H^+: SO_4^2 were found to be 1.00 ± 0.003: 0.0: 1.00 ± 0.005.

This would suggest the presence of $[Fe(SO_4)_2]^{2-}$ being the most likely Fe(II) complex and $[Fe(SO_4)_2]^-$ being the most likely complex formed with Fe(III) in the stripping solution.

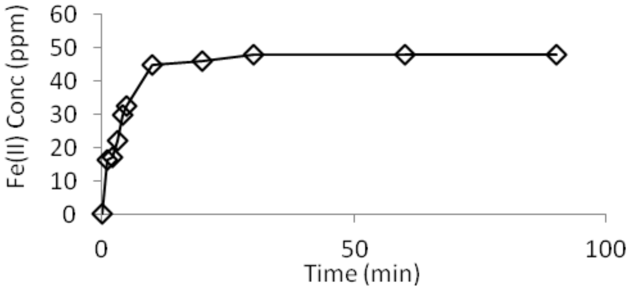

Figure 4.25 Back extraction curve for Fe(II) in deionised water.

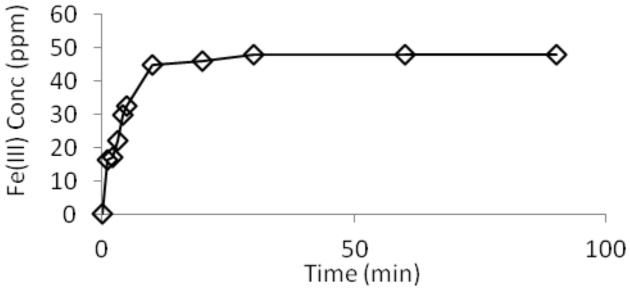

Figure 4.26 Back extraction curve for Fe(III) in deionised water

4.2.2.3 The postulation of the extracted species and mechanism of the membrane extraction from the equilibrium studies

The substitution of the counter-ion on the Aliquat 336 takes place by the following stoichiometric reaction:

$$2ACl + Na_2SO_4 \Leftrightarrow A_2SO_4 + 2NaCl \qquad \text{Eq. (21)}$$

The following stoichiometric equations describe the possible extraction processes involving the sulphate complexes that are formed. The most likely complex that will be formed is $[Co(SO_4)_2]^{2-}$ and this anion can form an ion-pair with the divalent Aliquat 336 cation according to the following stoichiometric equations:

$Co(SO_4)_2^{2-}{}_{S} + A_2SO_{4\,\mathbf{M}} \Leftrightarrow A_2Co(SO_4)_{\mathbf{2M}} + SO_4^{2-}{}_{S}$ Eq. (22)

$Co(SO_4)_3^{4-}{}_{S} + 2A_2SO_{4\,\mathbf{M}} \Leftrightarrow A_4Co(SO_4)_{\mathbf{3M}} + 2\ SO_4^{2-}{}_{S}$ Eq. (23)

The stripping will be described by the following stoichiometric equations:

$A_2Co(SO_4)_{\mathbf{2M}} \Leftrightarrow A_2SO_{4\,\mathbf{M}} + CoSO_4\mathbf{s}$ Eq. (24)

$A_4Co(SO_4)_{\mathbf{3M}} \Leftrightarrow 2A_2SO_{4\,\mathbf{M}} + CoSO_4\mathbf{s}$ Eq. (25)

A similar mechanism can be proposed for the nickel sulphate complex $[Ni(SO_4)_2]^{2-}$ and this cation can form an ion-pair with the monovalent Aliquat 336 cation according to the following stoichiometric equation:

$Ni(SO_4)_2^{2-}{}_{S} + A_2SO_{4\,\mathbf{M}} \Leftrightarrow A_2Ni(SO_4)_{\mathbf{2M}} + SO_4^{2-}{}_{S}$ Eq. (26)

It is probable that the stripping will be described by the following stoichiometric equation

$A_2Ni(SO_4)_{\mathbf{2M}} \Leftrightarrow A_2SO_{4\,\mathbf{M}} + NiSO_4\mathbf{s}$ Eq. (27)

The most likely complex that will be formed with Fe(II) is $[Fe(SO_4)_2]^{2-}$ and this cation can form an ion-pair with the divalent Aliquat 336 cation according to the following stoichiometric equations;

$Fe(SO_4)_2^{2-}{}_{S} + A_2SO_{4\,\mathbf{M}} \Leftrightarrow A_2Fe(SO_4)_{\mathbf{2M}} + SO_4^{2-}{}_{S}$ Eq. (28)

$Fe(SO_4)_3^{4-}{}_{S} + 2A_2SO_{4\,\mathbf{M}} \Leftrightarrow A_4Fe(SO_4)_{\mathbf{3M}} + 2\ SO_4^{2-}{}_{S}$ Eq. (29)

It is probable that the stripping will be described by:

$A_2Fe(SO_4)_{\mathbf{2M}} \Leftrightarrow A_2SO_{4\,\mathbf{M}} + FeSO_4\mathbf{s}$ Eq. (30)

$A_4Fe(SO_4)_{\mathbf{3M}} \Leftrightarrow 2A_2SO_{4\,\mathbf{M}} + F\mathbf{e}SO_4\mathbf{s}$ Eq. (31)

The extracted species for the equilibrium studies for Fe(III) can also be proposed.

The plausible complex that will be formed with Fe(III) is $[Fe(SO_4)_2]^-$ and this cation can form an ion-pair with the divalent Aliquat 336 cation according to the following stoichiometric equations;

$$Fe(SO_4)_2^-{}_{\mathbf{S}} + A_2SO_{4\,\mathbf{M}} \Leftrightarrow 2\ AFe(SO_4)_{2\mathbf{M}} + SO_4^{2-}{}_{\mathbf{S}} \qquad \text{Eq. (32)}$$

It is likely the stripping will be described by:

$$2\ AFe(SO_4)_{2\mathbf{M}} \Leftrightarrow A_2SO_{4\,\mathbf{M}} + Fe_2(SO_4)_{3\mathbf{S}} \qquad \text{Eq. (33)}$$

4.2.3 Membrane extraction studies of Co(II), Ni(II), Fe(II) and Fe(III) from nitric acid

4.2.3.1 The influence of nitric acid concentration on the extraction

As in the previous studies for the extraction of Co(II) from acidic media the optimum membrane of 40% (w/w) Aliquat 336/PVC was established and then used in the extraction experiments. The counter-ion on the Aliquat 336 being replaced with nitrate as has been discussed in Chapter Three.

Studies were done to establish the optimum concentration of nitric acid (HNO_3) for the extraction studies and it was found that the optimum extraction of Co(II) occurred at a concentration of 2.0M nitric acid as can be seen in Figure 4.27.

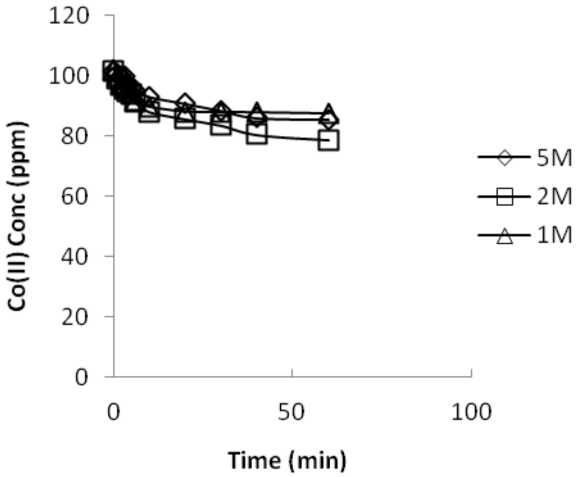

Figure 4.27. Concentration vs. time curves for the extraction of 100ppm Co(II) in 5M, 3M and 1M HNO_3 solutions using the 40%(w/w) Aliquat 336/PVC membranes.

Initial studies were also carried out to find the optimum concentration of nitric acid for the extraction of Ni(II). Solutions that contained 100ppm of Ni(II) in 5.0M, 2.0M and 1.0M nitric acid were prepared and the extraction curves obtained using the 40% (w/w) Aliquat 336/PVC membrane and it was determined the the optimal extraction occurred in 1M nitric acid. Solutions that contained 100ppm Fe(II) and Fe(III) were prepared in varying concentrations of nitric acid that ranged from 5.0M to 1.0M. The extraction curves were obtained and it was found that the maximum extraction of both the Fe(II) and Fe(III) occurred at a concentration of 3.0M nitric acid.

4.2.3.2 Back extraction studies

Back extraction studies using different concentrations of nitric acid (1.0M, 0.5M and 0.1M) and deionised water showed that the Co(II) was completely stripped using deionised water in a similar time frame to the initial extraction time.

Equilibrium studies [63, 64, 86] were done for the extraction of Co(II)) from 2M nitric acid. The analysis of Co(II) was carried out by atomic absorption spectrometry and the nitrate analysis was done by titration using a modified Leithe procedure [133] and the concentration of the hydrogen ion in the stripping solution was measured potentiometrically using a hydrogen ion electrode. The ratios of Co(II) :H+: NO_3^- in the stripping solution was found to be 1.00 ± 0.05 : 0.00 ± 0: 00: 3.00 ± 0.05 which would imply that the nitrate complex formed in the membrane matrix was $[Co(NO_3)_4]^{2-}$.

Back extraction studies using 2.0M, 1.0M nitric acid and deionised water were carried out, and it was found that the nickel(II) was completely stripped from the membrane when deionised water was used. In order to ascertain the probable species involved in the reaction mechanism, the stripping solution was analysed for Ni(II) by atomic absorption spectrometry. The nitrate ion was determined by titration using a modified Leithe procedure [135] and the concentration of the hydrogen ion in the stripping solution was measured potentiometrically, using a hydrogen ion electrode. The ratios of Ni(II) :H^+: NO_3^- was found to be 1.00 ± 0.05 : 0.00 ± 0: 00: 3.00 ± 0.05 , implying that the nitrate complex formed in the membrane matrix was $[Ni(NO_3)_4]^{2-}$.

Back extraction studies for iron(II) and iron(III) were carried out in deionised water and the back extraction curves showed that in each case the metal is completely stripped from the membrane using deionised water. The stripping solution was analysed for the presence of iron(II) and iron(III), hydrogen ion and nitrate ion as has been previously described [135].

For Fe(II) the ratios of Fe^{2+}: H^+: NO_3^- were found to be 1.00 ±0.003: 0.0: 3.00 ±005 and for Fe(III) the ratios of Fe^{3+}: H^+: NO_3^- were found to be 1.00 ± 0.003: 0.0: 4.00 ± 0.005 . These results would suggest the presence of $[Fe(NO_3)_3]^-$ and $[Fe(NO_3)_4]^-$ respectively being formed in the membrane matrix.

4.2.3.3 The postulation of the extracted species and mechanism of the membrane extraction from the equilibrium studies

The substitution of the counter-ion on the Aliquat 336 takes place by the following stoichiometric reaction:

$$ACl + NaNO_3 \Leftrightarrow ANO_3 + NaCl \qquad \text{Eq. (34)}$$

It has been established [63, 65, 86] that the corresponding negatively charged metal-nitrate complexes formed an ion-pair with the Aliquat 336 cation at the membrane/solution interface. This ion-pair was subsequently extracted into the bulk of the membrane. A similar mechanism can be proposed for the extraction of Co(II) from its nitrate aqueous solutions. In the presence of the nitrate ion Co(II) can form four nitrate complexes, $Co(NO_3)_i^{2-i}$ where i=1,2,3,4. Only two of these complexes are negatively charged and can form an ion-pair with the monovalent Aliquat 336 cation according to the following stoichiometric equations:

$Co(NO_3)_3^-{}_S + ANO_3 \Leftrightarrow ACo(NO_3)_{3M} + NO_3-$ Eq. (35)

$Co(NO_3)_4^{2-}{}_S + ANO_3 \Leftrightarrow A_2Co(NO_3)_{4M} + 2NO_3-$ Eq. (36)

It is probable that stripping will be described by the following stoichiometric equations:

$ACo(NO_3)_{3M} \Leftrightarrow ANO_{3M} + Co(NO_3)_{2S}$ Eq. (37)

$A_2Co(NO_3)_{4M} \Leftrightarrow 2ANO_{3M} + Co(NO_3)_{2S}$ Eq. (38)

A similar mechanism can be proposed for the extraction of Ni(II) from its aqueous nitrate solutions. In the presence of the nitrate ion Ni(II) can form 4 nitrate complexes, $Ni(NO_3)_i^{2-i}$ where i=1,2,3,4. Only two of these complexes are negatively charged and can form an ion-pair with the monovalent Aliquat 336 cation according to the following stoichiometric equations:

$Ni(NO_3)_3^-{}_S + ANO_3 \Leftrightarrow ANi(NO_3)_{3M} + NO_3^-$ Eq. (39)

$Ni(NO_3)_4^{2-}{}_S + ANO_3 \Leftrightarrow A_2Ni(NO_3)_{4M} + 2NO_3^-$ Eq. (40)

Stripping will be described by the following stoichiometric equations:

$ANi(NO_3)_{3M} \Leftrightarrow ANO_{3M} + Ni(NO_3)_{2S}$ Eq. (41)

$A_2Ni(NO_3)_{4M} \Leftrightarrow 2ANO_{3M} + Ni(NO_3)_{2S}$ Eq. (42)

The proposed mechanism is in agreement with that described by Buch *et al*. [90, 91] for the mechanism of the extraction of nickel using 2-ethylhexanal oxime in solutions with low acid concentration in nitrate media. A similar mechanism can be proposed for the extraction of Fe(II) from its nitrate aqueous solutions. In the presence of the nitrate ion Fe(II) can form 4 nitrate complexes, $[Fe(NO_3)_i]^{2-i}$ where i=1,2,3,4. Only two of these complexes are negatively charged and can form an ion-pair with the monovalent Aliquat 336 cation according to the following stoichiometric equations:

$Fe(NO_3)_3{}^-{}_S + ANO_3 \Leftrightarrow AFe(NO_3)_{3M} + NO_3{}^-$ Eq. (43)

$Fe(NO_3)_4{}^{2-}{}_S + ANO_3 \Leftrightarrow A_2Fe(NO_3)_{4M} + 2NO_3{}^-$ Eq. (44)

Most likely stripping will be described by the following stoichiometric equations:

$AFe(NO_3)_{3M} \Leftrightarrow ANO_{3M} + Fe(NO_3)_{2S}$ Eq..(45)

$A_2Fe(NO_3)_{4M} \Leftrightarrow 2ANO_{3M} + Fe(NO_3)_{2S}$ Eq. (46)

For Fe(III) the most likely negatively charged complex that is formed is $[Fe(NO_3)_4]^-$
and can form an ion-pair with the monovalent Aliquat 336 cation according to the following stoichiometric equations:

$Fe(NO_3)_4{}^-{}_S + ANO_3 \Leftrightarrow AFe(NO_3)_{4M} + NO_3$- Eq. (47)

$Fe(NO_3)_6{}^{3-}{}_S + 3ANO_3 \Leftrightarrow A_3Fe(NO_3)_{6M} + 3NO_3$- Eq. (48)

The stripping will be described by the following stoichiometric equations:

$$AFe(NO_3)_{4M} \Leftrightarrow ANO_{3M} + Fe(NO_3)_{3S} \qquad \text{Eq. (49)}$$

$$A_3Fe(NO_3)_{6M} \Leftrightarrow 3ANO_{3M} + Fe(NO_3)_{3S} \qquad \text{Eq. (50)}$$

In this section it has been shown that the membrane extraction of cobalt(II) was carried out successfully from a range of concentrations of nitric acid that ranged from 5.0M to 1.0M with the optimum extraction occurring at a concentration of 2.0M nitric acid. The Co(II) was completely stripped from the membrane in deionised water and a chemical analysis was done to obtain the ratios of cobalt(II) and nitrate ions that were present. A mechanism was proposed where it was determined that the most likely species that is extracted into the membrane is $[Co(NO_3)_4]^{2-}$. This is supported by the ratios obtained for cobalt and nitrate in the back extraction studies. The extraction process occurred in a similar time frame to that done for the extraction in chloride media and it is likely that the cobalt tetranitro complex formed is tetrahedral in structure. The mechanism and extraction in this monovalent acidic medium appears to follow a similar path to that already seen in the extraction of cobalt(II) in hydrochloric acid and in other chloride media.

Nickel(II) was successfully extracted from nitrate solutions using 1.0 M nitric acid and the 40% (w/w) Aliquat 336/PVC membrane. The Ni(II) was able to be completely back extracted in deionised water. A mechanism for the extraction process was proposed and the mechanism shows good agreement with that demonstrated in earlier studies [90, 91].

Fe(II) and Fe(III) are shown to have a maximum extractability in 3.0M in nitric acid solutions and can be completely stripped from the membrane using deionised water. A mechanism for each extraction is proposed.

4.2.4 Membrane extraction studies of Co(II) from oxalate solution

4.2.4.1 The effect of concentration on the extraction of Co(II)

As in the previous studies for the extraction of Co(II) from acidic media the optimum membrane of 40% (w/w) Aliquat 336/PVC was established and then used in the extraction experiments. For these studies the counter-ion on the Aliquat 336 was replaced with oxalate as described earlier in Chapter Three.

Studies were carried out to establish the optimum concentration of sodium oxalate ($Na_2C_2O_4$) to maximise the efficiency of extraction of cobalt(II). From previous studies [86] it has been established that the optimum extractability occurs at a pH of 6.7 and the oxalate ion $[C_2O_4]^{2-}$ is the predominant species present in solution. The concentration of the sodium oxalate solution was determined by titration against a standard potassium permanganate solution. Although for consistency oxalic acid was used in these extraction experiments, the previous studies provided a reasonable indication of the possible suitable range of concentrations. The optimum extraction of Co(II) took place in 0.2M oxalic acid as can be seen in Figure 4.28.

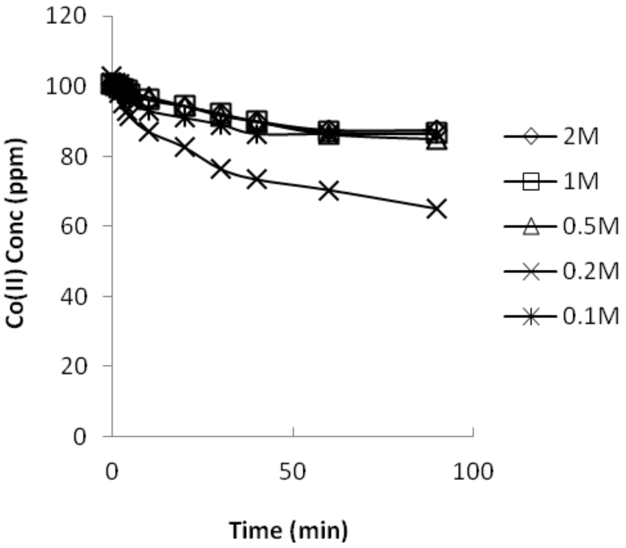

Figure 4.28. Concentration vs. time curves for the extraction of 100PPM Co(II) in 2.0M, 1.0M and 0.5M, 0.2M and 0.1M $H_2C_2O_4$ solutions using the 40% (w/w) Aliquat 336/PVC membrane.

4.2.4.2 Back extraction studies

Back extraction studies using different concentrations of oxalic acid (1.0M, 0.5M and 0.1M) and deionised water showed that the Co(II) was completely stripped using deionised water in a similar time frame to the initial extraction time. Equilibrium studies [63, 64, 86] were carried out for the extraction of Co(II)) from 0.2M oxalic acid. The analysis of Co(II) was carried out by atomic absorption spectrometry and the oxalate analysis was carried out by titration using a standard potassium permanganate solution [135], the concentration of the hydrogen ion in the stripping solution was measured potentiometrically using a hydrogen ion electrode. The ratios of Co(II) :H+: $C_2O_4^{2-}$ was found to be 1.00 ± 0.05 : 0.00 ± 0: 00: 1.00 ± 0.05, implying that the complex in the membrane matrix was $[Co(C_2O_4)_2]^{2-}$.

4.2.4.3 The postulation of the extracted species and mechanism of the membrane extraction from the equilibrium studies

The substitution of the counter-ion on the Aliquat 336 takes place by the following stoichiometric reaction:

$$2ACl + Na_2C_2O_4 \Leftrightarrow A_2\,C_2O_4 + 2NaCl \qquad \text{Eq. (51)}$$

It has been established that the corresponding negatively charged metal-oxalate ion-pair formation with the Aliquat 336 cation at the membrane/solution interface[86]. This ion-pair was subsequently extracted into the bulk of the membrane. A similar mechanism can be proposed for the extraction of Co(II) from its oxalate aqueous solutions. In the presence of the oxalate ion Co(II) can form two oxalate complexes, $[Co(C_2O_4)_2]^{2-}$ and $[Co(C_2O_4)_3]^{4-.}$ Both of these complexes are negatively charged and can form an ion-pair with the divalent Aliquat 336 cation according to the following stoichiometric equations:

$$Co(C_2O_4)_2^{2-}{}_{S} + A_2C_2O_{4\,M} \Leftrightarrow A_2Co(C_2O_4)_{2\,M} + C_2O_4^{2--}{}_{S} \qquad \text{Eq. (52)}$$

$$Co(C_2O_4)_3^{4-}{}_{S} + 2A_2C_2O_{4\,M} \Leftrightarrow A_4Co(C_2O_4)_3^{\cdot}{}_{M} + 2\,C_2O_4^{2--}{}_{S} \qquad \text{Eq. (53)}$$

.

Most likely stripping will be described by the following stoichiometric equation:

$$A_2Co(C_2O_4)_{2\,\mathbf{M}} \Leftrightarrow A_2C_2O_{4\,\mathbf{M}} + Co(C_2O_4)\mathbf{s} \qquad \text{Eq. (54)}$$

$$A_4Co(C_2O_4)_{3}^{\cdot}{}_{\mathbf{M}} \Leftrightarrow 2A_2C_2O_{4\,\mathbf{M}} + Co(C_2O_4)\mathbf{s} \qquad \text{Eq. (55)}$$

Cobalt(II) was successfully extracted from oxalic acid solution and the cobalt(II) was able to be completely stripped from the membrane in deionised water. A mechanism is proposed with the most likely species that is extracted into the membrane being $[Co(C_2O_4)_2]^{2-}$ and this is supported by the ratios of cobalt(II) and oxalate ion that was determined in the stripping solution and is further supported by studies that were done earlier by Paimin and Cattrall [86]. The time frame for the extraction was similar to that obtained in previous studies to that for the divalent sulphate ion.

4.3 Conclusion

This Chapter has demonstrated the viability of the Aliquat 336 /PVC membrane as an effective tool for the membrane extraction of cobalt(II), nickel(II), iron(II) and iron(III) from a variety of aqueous solutions.

Clearly, the membrane is more effective when a quaternary ammonium salt is used as the extractant as compared with a primary, secondary or tertiary amine. The best results were obtained when 40% (w/w) Aliquat 336 was combined with PVC to form the membrane.

The membrane extraction process for each metal was also seen to be dependent on the concentration of the anion in the media that was used and this is in agreement with the literature studies that were discussed in the early sections of this thesis.

The optimum results for the membrane extraction of cobalt(II) was found to occur in solutions of 7.0M hydrochloric acid, 2.0M sulphuric acid, 2.0M nitric acid and 0.2M oxalic acid, those for nickel(II) were found to take place in 1.0M hydrochloric acid, 1.0M sulphuric acid, 1.0M nitric acid and the membrane extraction of iron(II) and iron(III) in 3.0M hydrochloric acid, 3.0M sulphuric acid, 3.0M nitric acid.

For each of the media used the extracted species in the equilibrium studies has been postulated and supported by evidence from back extraction studies as well as literature studies and these extraction processes described as "mechanisms" are similar for each of the metal ions that were studied. This is not unexpected as the three transition metals that were studied all have similar chemical properties.

There were further similarities found for the extracted species in the equilibrium studies that were postulated for the membrane extraction of the metals in monovalent chloride media and nitrate media and for the membrane extraction of the metals in the divalent sulphate media and oxalate media. The work that was completed in this section will provide the basis for the unique selective extraction of each of these metals in aqueous chloride, sulphate and nitrate media using the Aliquat 336/PVC membrane.

The following Chapter will present the selective separation of cobalt from nickel in aqueous media and the selective separation of cobalt from nickel and iron in a variety of aqueous media that includes chloride, sulphate and nitrate.

Chapter Five

Selective separation and extraction of Cobalt(II), Nickel(II), Iron(II) and Iron(III) in aqueous media

5.1 Introduction

The selective separation and extraction of cobalt(II) and nickel(II) has been an existing problem for many years. There have been many attempts, many of them involving the use of organic extractants and volatile and hazardous solvents that can often pose environmental disposal problems. The need for the development of an extraction system from aqueous solutions such industrial wastewaters, that can also separate and extract these metals without the need for organic solvents is imperative in a world where pollution and dwindling resources are becoming even more important. The ability to separate these three metals from each other in aqueous solutions by membrane extraction is an unique solution to this problem.

What follows in this Chapter are detailed descriptions of the extraction and stripping experiments that were conducted. The studies that have been addressed are listed below with the relevant sections in which they can be located in this Chapter.

(i) the separation of cobalt(II) from nickel(II) in hydrochloric acid (5.2.1.1)
(ii) the separation of nickel(II) from cobalt(II) in hydrochloric acid (5.2.2.1)
(iii) the separation of cobalt(II) from nickel(II) in sulphate media (5.2.9.1)
(iv) the separation of nickel(II) from cobalt(II) in sulphate media (5.2.9.2)
(v) the separation of cobalt(II) from nickel(II), iron(II) and iron(III) in sulphate media (5.2.9.3 and 5.2.9.4)
(vi) the separation of cobalt(II) from nickel(II) in nitrate media (5.2.10.1)
(vii) the separation of nickel(II) from cobalt(II) in nitrate media (5.2.10.2)
(viii) the separation of iron(II) and iron(III) from cobalt(II) and nickel(II) in nitrate media (5.2.10.3 and 5.2.10.4)

Firstly the selective separation and extraction of cobalt and nickel in aqueous chloride, sulphate and nitrate media is discussed and then the selective separation and extraction of cobalt, nickel and iron is shown from the same range of aqueous media.

5.2 Results and Discussion

5.2.1 Selective separation studies of Co(II), Ni(II), Fe(II) and Fe(III) in aqueous chloride media

5.2.1.1 Selective separation studies of Co(II) from Ni(II) in hydrochloric acid

The previous extraction studies of cobalt(II) and nickel(II) in Chapter Four indicated that optimum extraction occurred whilst using a membrane that contained 40% Aliquat 336/PVC (w/w) and this membrane was therefore used for the following studies. It was also determined that the maximum extraction of Co(II) into the membrane occurred in solutions of 7.0 M hydrochloric acid, whilst the maximum extraction of Ni(II) occurred in solutions of 1.0 M HCl.

Studies were carried out with solutions containing 110ppm Co(II) and 109ppm Ni(II) in 7.0M HCl using the two- compartment vessel as previously described in Chapter Three. The feed solution was introduced on each side of the membrane that was placed between the compartments and held together with a Teflon seal. Aliquots of the feed solution were removed on a regular basis and analysed by atomic absorption spectroscopy for metal ion content. Figure 5.1 shows the extraction curves that were obtained.

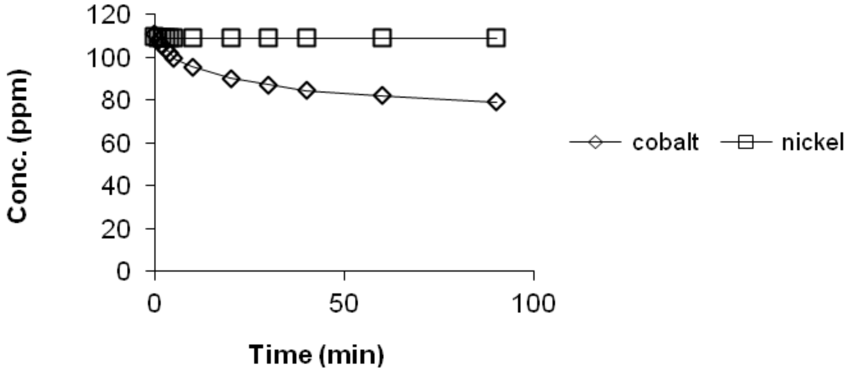

Figure 5.1. Concentration vs. time curves for the selective extraction from a feed solution containing 110ppm Co(II) and 109ppm Ni(II) in 7.0M HCl

As can be seen from Figure 5.1, at this chloride concentration the cobalt(II) is preferentially separated and extracted from the nickel(II). The same separation and extraction using a single cell had a very similar extraction curve to this and it is suggested that either system can be used for the selective separation of Co(II) from Ni(II). This is the first time that cobalt-nickel separation has been completed using an Aliquat 336/PVC membrane. It was also confirmed that the amount of Co(II) extracted on to the membrane was not affected by the presence of Ni(II) ions in solution.

5.2.2 Selective separation studies of Ni(II) from Co(II) in chloride media

5.2.2.1 Selective separation studies of Ni(II) from Co(II) in hydrochloric acid

In the previous extraction studies it was found that the optimum extraction occurred whilst using a membrane that contained 40% (w/w) Aliquat 336/PVC. This membrane was used for the following studies. It was also previously determined that the maximum extraction of Ni(II) into the membrane occurred in solutions of 1.0 M hydrochloric acid.

Studies were done with solutions containing 100ppm Co(II) and 100ppm Ni(II) in 1.0M HCl using the two-compartment vessel. Figure 5.2 shows the extraction curves obtained.

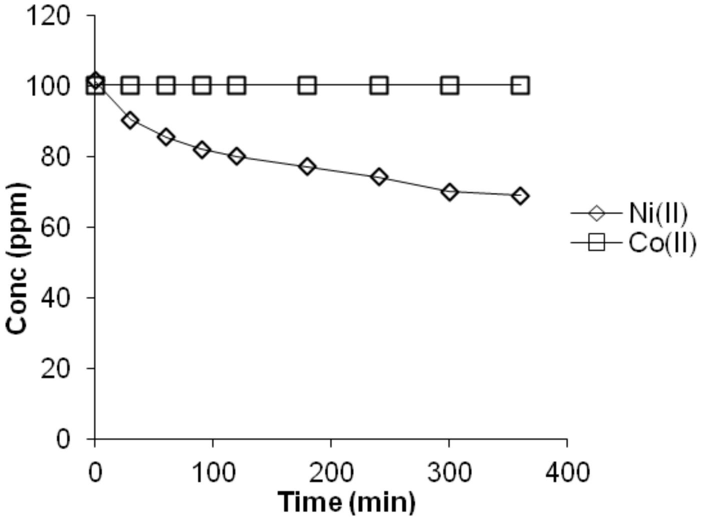

Figure 5.2. Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Ni(II) and 100ppm Co(II) in 1.0M HCl.

It can be seen from Figure 5.2 that the Co(II) remains in the feed phase whilst the Ni(II) is extracted in 1.0M HCl

These studies represent the first time that the Aliquat 336/PVC membrane has been shown to be an effective method of membrane extraction for the selective separation and extraction of Co(II) from Ni(II), and Ni(II) from Co(II) using a variety of chloride media.

5.2.3 Selective separation of Co(II) from Ni(II) and Fe(II)

5.2.3.1 Selective separation of Co(II) from Ni(II) and Fe(II) in hydrochloric acid

From the previous experimental studies that were outlined in Chapter Four, to increase the capability of the system and to make the findings more applicable to industrial conditions, it was ascertained that the extraction of Co(II) was maximized in hydrochloric acid that had a concentration of 7.0.M. This was further established in the selective separation of Co(II) from Ni(II) that was achieved under the same condition.

Fe(II) is now added to the feed mixture in order to investigate whether or not the presence of a third transition metal alters the selective nature of the separation and extraction of cobalt(II).

Figure 5.3 shows the extraction curves obtained using the 40% (w/w) Aliquat 336/PVC membrane for a feed solution that contains 100ppm Co(II), 100ppm Ni(II) and 100ppm Fe(II).

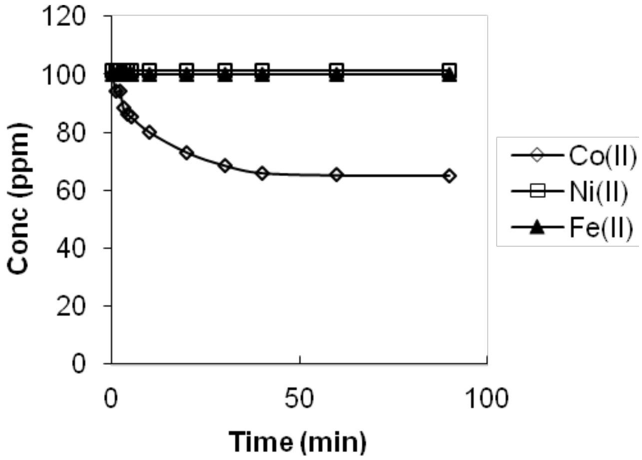

Figure 5. 3. Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Co(II) from 100ppm Ni(II) and 100ppm Fe(II) in 7.0M HCl

It can be seen from the extraction curves in Figure 5.3, that the Co(II) is preferentially and selectively separated and extracted from both the Ni(II) and Fe(II) in the feed solution where the metal ions are in 7.0M hydrochloric acid solution and when the two compartment vessel was used.

Cobalt(II) was seen to be selectively extracted from a feed solution that contained three transition metals, namely: cobalt(II), nickel(II) and iron(II) in a variety of chloride media. More studies were done with the same chloride media that was used in the single metal extraction work with very similar results. It can therefore be deemed that the membrane system is highly selective for cobalt(II) when a variety of chloride media is used.

5.2.4 Selective separation of Co(II) from Ni(II) and Fe(III)

5.2.4.1 Selective separation of Co(II) from Ni(II) and Fe(III) in hydrochloric acid

From the previous experimental studies that were outlined in Chapter Four it was ascertained that the extraction of Co(II) was maximized in hydrochloric acid that had a concentration of 7.0M. This was further established in the selective separation of Co(II) from Ni(II) which was achieved under the same conditions. Fe(III) is now added to the feed mixture and replaces Fe(II) in order to investigate whether or not the presence of a third transition metal with a different (higher) oxidation state has any affect on the selective separation and extraction of cobalt(II).

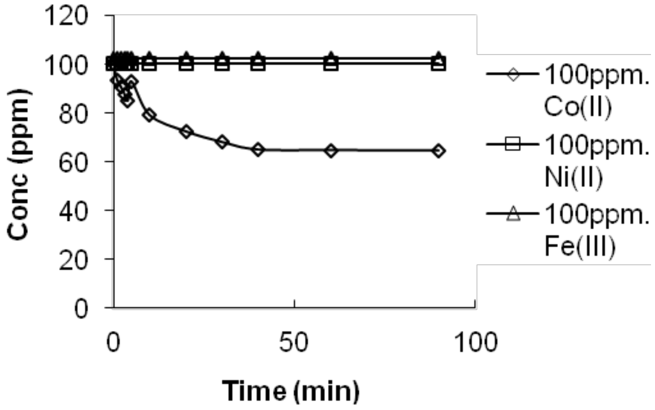

Figure 5. 4. Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Co(II) from 100ppm Ni(II) and 100ppm Fe(III) in 7.0M HCl

It can be seen from the extraction curves in Figure 5.4 that the Co(II) is preferentially and selectively separated from both the Ni(II) and Fe(III) in the feed solution where the metal ions are in 7.0M hydrochloric acid solution when the two compartment cell was used. There was very little difference in the extraction curves for the two- compartment and single vessel extraction showing that the selective separation can still be successfully completed in 7.0M hydrochloric acid in either environment.

The extraction curves that were obtained for the selective separation of cobalt(II) in feed solutions that contained Fe(II) are very similar to those that were obtained for feed solutions where the iron(II) were replaced by iron(III). The oxidation state of iron does not seem to make any difference to the selective separation of cobalt(II).

5.2.5 Selective separation of Ni(II) from Co(II) and Fe(II)

5.2.5.1 Selective separation of Ni(II) from Co(II) and Fe(II) in hydrochloric acid

In Chapter Four it was determined that the best extractability of nickel(II) occurred at a concentration of 1.0M hydrochloric acid and this was shown again in the separation of Ni(II) from Co(II) earlier in this Chapter. Figure 5.5 shows the extraction curves that were obtained for a feed solution containing 100ppm Ni(II), 100ppm Co(II) and 100ppm Fe(II) in 1.0M HCl.

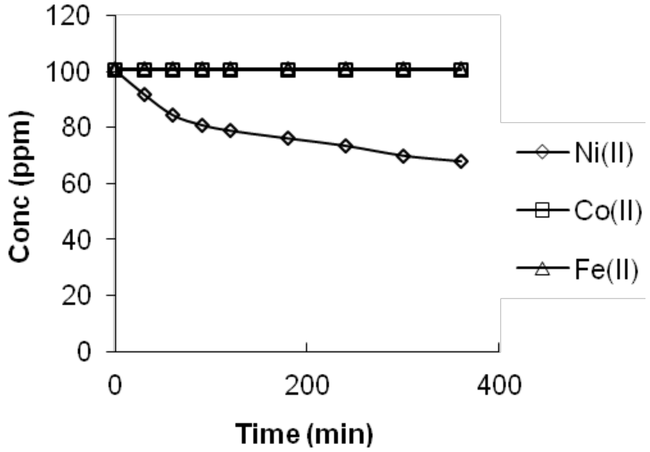

Figure 5.5 Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Ni(II) from 100ppm Co(II) and 100ppm Fe(II) in 1.0M HCl

Figure 5.5 shows that the Ni(II) is selectively separated and extracted from a feed solution containing Ni(II), Co(II) and Fe(II) in 1.0M hydrochloric acid.

It can now be deemed that nickel(II) can be selectively extracted from a feed solution that contains nickel(II), cobalt(II), and iron(II) in a variety of chloride media. It is reasonable to assume that the extracted species for the extraction is the same as that previously proposed based on the mole ratios that were obtained for the back extraction studies. The membrane can be completely stripped of the nickel(II) in deionised water.

5.2.6 Selective separation of Ni(II) from Co(II) and Fe(III)

5.2.6.1 Selective separation of Ni(II) from Co(II) and Fe(III) in hydrochloric acid

The selective separation where the feed solution now contains the iron in a different (higher) oxidation state is now investigated using the same criteria.

In Chapter Four it was determined that the best extractability of nickel(II) occurred at a concentration of 1.0M hydrochloric acid and this was shown again in the separation of Ni(II) from Co(II). Figure 5.6 shows the extraction curve that was obtained for a feed solution containing 100ppm Ni(II), 100ppm Co(II) and 100ppm Fe(III) in 1.0M HCl.

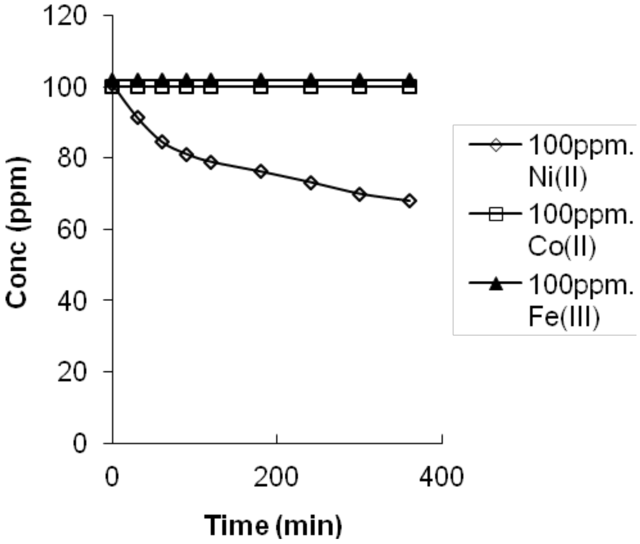

Figure 5. 6. Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Ni(II) from 100ppm Co(II) and 100ppm Fe(III) in 1.0M HCl

Figure 5.6 shows that the Ni(II) is selectively separated and extracted from the feed solution containing the cations Ni(II), Co(II) and Fe(III) in 1.0M hydrochloric acid.

It has been demonstrated that nickel(II) can be selectively extracted from a feed solution that contains the cations nickel(II), cobalt(II), and iron(III) in a variety of chloride media. It is reasonable to assume that the extracted species for the extraction is the same as that previously proposed based on the results of the back extraction studies that were completed. The membrane can be completely stripped in deionised water.

5.2.7 Selective separation of Fe(II) from Co(II) and Ni(II)

5.2.7.1 Selective separation of Fe(II) from Co(II) and Ni(II) in hydrochloric acid

The maximum extraction of Fe(II) was found to take place in 3.0M hydrochloric acid as was discussed in Chapter Four.

Figure 5.7 shows the extraction curves for the selective separation and extraction of Fe(II) from Co(II) and Ni(II) in 3.0M HCl.

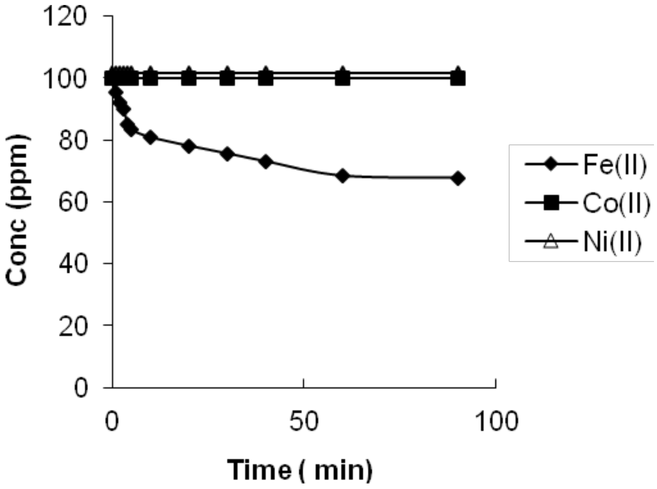

Figure 5.7. Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Fe(II) from 100ppm Co(II) and 100ppm Ni(II) in 3.M HCl

At a concentration of 3.0M hydrochloric acid the iron(II) is selectively separated and extracted from cobalt(II) and nickel(II).

5.2.8 Selective separation of Fe(III) from Co(II) and Ni(II)

5.2.8.1 Selective separation of Fe(III) from Co(II) and Ni(II) in hydrochloric acid

The maximum extraction of Fe(III) was found to take place in 3.0M hydrochloric acid as was discussed in Chapter Four. Figure 5.8 shows the extraction curves for the selective separation and extraction of Fe(III) from Co(II) and Ni(II) in 3.0M HCl.

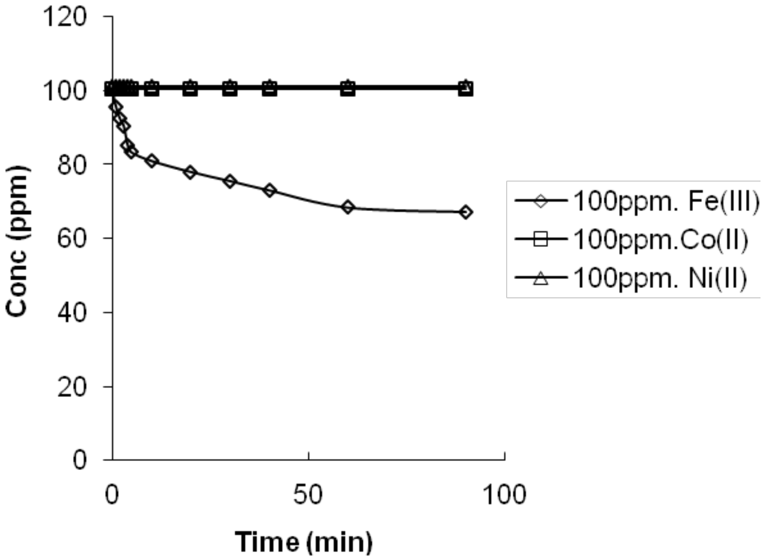

Figure 5.8. Concentration vs. time curves for the selective separation from a feed solution containing 100ppm Fe(III) from 100ppm Co(II) and 100ppm Ni(II) in 3.0M HCl

It can be deemed that at a concentration of 3.0M hydrochloric acid the iron(III) is selectively separated and extracted from the cations cobalt(II) and nickel(II).

5.2.9 Selective separation studies of Co(II), Ni(II), Fe(II) and Fe(III) in sulphuric acid

5.2.9.1 Selective separation of Co(II) from Ni(II) in sulphuric acid

As has been previously described in Chapter Three the counter ion on the Aliquat 336/PVC membrane was changed from the chloride group to that of the sulphate group and it was these ion -pair changed membranes that were used for the selective separation and extraction and back extraction experiments in sulphate media.

From the previous extraction studies of cobalt(II) and nickel(II) it was found that the optimum extraction occurred whilst using a membrane that contained 40% (w/w) Aliquat 336/PVC. This membrane was used for the following studies. It was also determined that the maximum extraction of Co(II) into the membrane occurred in solutions of 2.0 M sulphuric acid and the maximum extraction of Ni(II) occurred in solutions of 1.0 M sulphuric acid. Figure 5.9 shows the extraction curve that was obtained for the selective separation and extraction of Co(II) from Ni(II) in 2.0M sulphuric acid.

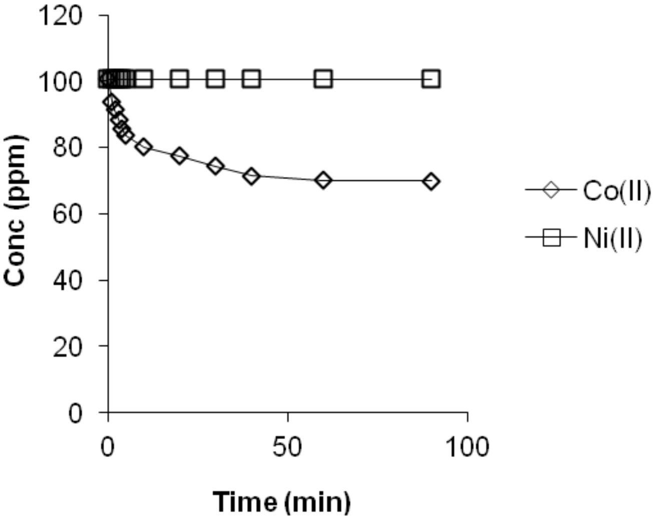

Figure 5.9. Concentration vs. time curves for the selective separation from a feed solution containing Co(II) from Ni(II) in 2.0M sulphuric acid

As can be seen from Figure 5.9 for a feed solution containing 100ppm Co(II) and 100ppm Ni(II) in 2.0M sulphuric acid the cobalt(II) is selectively separated from the nickel(II) which remains in the feed solution.

5.2.9.2 Selective separation of Ni(II) from Co(II) in sulphuric acid

In Chapter Four, it was established that the optimum extractability of nickel(II) occurred in 1.0M sulphuric acid. Figure 5.10 shows the extraction curve for a feed solution containing 100ppm Ni(II) and 100ppm Co(II) in 1.0M sulphuric acid

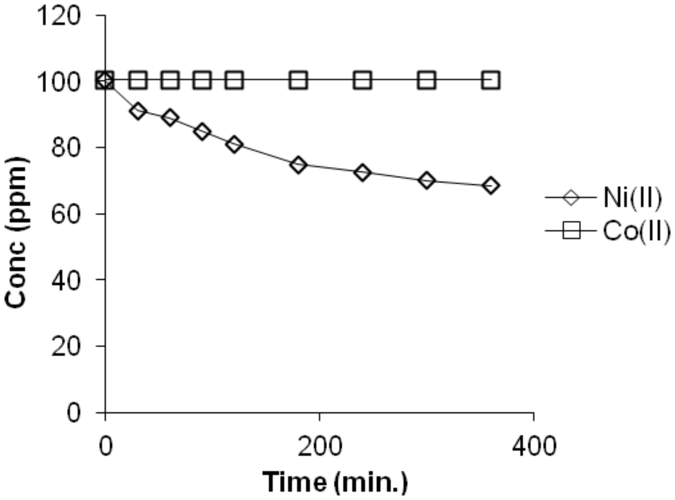

Figure 5.10. Concentration vs. time curves for the selective separation of Ni(II) from Co(II) from a feed solution containing Ni(II) and Co(II) in 1.0M sulphuric acid

It can be seen from the extraction curve in Figure 5.10 that the Ni(II) is selectively separated and extracted into the membrane and the Co(II) concentration remains the same as it was in the initial feed solution.

5.2.9.3 Selective separation of Fe(II) from Co(II) and Ni(II) in sulphuric acid

In Chapter Four, it was established that Co(II) could be extracted in 2.0M sulphuric acid, Ni(II) in 1.0M sulphuric acid and Fe(II) in 3.0M sulphuric acid. A solution containing 100ppm Co(II), 100ppm Ni(II) and 100ppm Fe(II) was prepared and the 40% (w/w) Aliquat/PVC membrane used for membrane extraction, Figure 5.11 shows the extraction curve that was obtained.

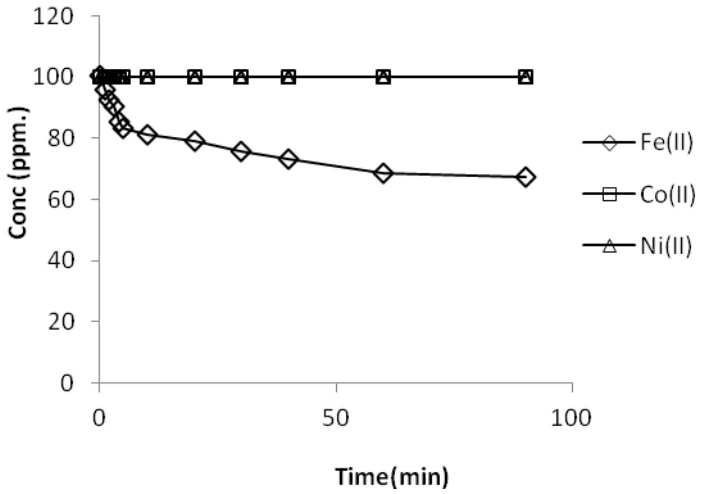

Figure 5.11. Concentration vs. time curves for the selective separation of Fe(II) from Co(II) and Ni(II) from a feed solution containing Fe(II), Co(II) and Ni(II) in 3.0M sulphuric acid

As can be seen from Figure 5.11, iron(II) is selectively extracted from solution whilst the cobalt(II) and nickel(II) remains in solution.

5.2.9.4 Selective separation of Fe(III) from Co(II) and Ni(II) in sulphuric acid

In Chapter Four, it was established that Co(II) could be extracted in 2.0M sulphuric acid, Ni(II) in 1.0M sulphuric acid and Fe(III) in 3.0M sulphuric acid. A solution containing 100ppm Co(II), 100ppm Ni(II) and 100ppm Fe(III) was prepared and the 40% (w/w)Aliquat/ PVC membrane used for membrane extraction, Figure 5.12 shows the extraction curve that was obtained.

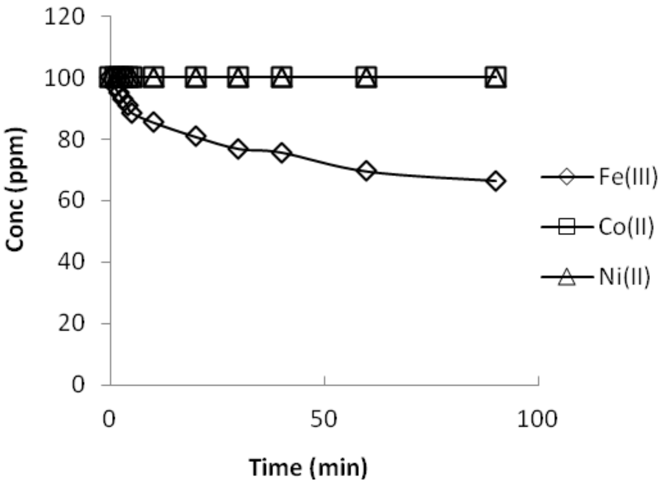

Figure 5.12 Concentration vs. time curves for the selective separation of Fe(III) from Co(II) and Ni(II) from a feed solution containing Fe(III), Co(II) and Ni(II) in 3.0M sulphuric acid

As can be seen from Figure 5.12, iron(III) is selectively extracted from solution whilst the cobalt(II) and nickel(II) remains in solution.

5.2.10 Selective separation studies of Co(II), Ni(II) , Fe(II) and Fe(III)from nitric acid

5.2.10.1 Selective separation of Co(II) from Ni(II) in nitric acid

As has been previously described in Chapter Three, the counter ion on the Aliquat 336/PVC membrane was changed from the chloride group to the nitrate group and it was these membranes with the changed ion-pairs that were used for the selective separation and extraction and back extraction experiments.

From the previous extraction studies of cobalt(II) and nickel(II) it was found that the optimum extraction occurred whilst using a membrane that contained 40% (w/w) Aliquat 336/PVC, This membrane was used for the following studies. It was also determined that the maximum extraction of Co(II) into the membrane occurred in solutions of 2.0 M nitric acid and the maximum extraction of Ni(II) occurred in solutions of 1.0 M nitric acid as has been discussed in Chapter Four. Figure 5.13 shows the extraction curve that was obtained for the selective separation and extraction of Co(II) from Ni(II) in 2.0M nitric acid.

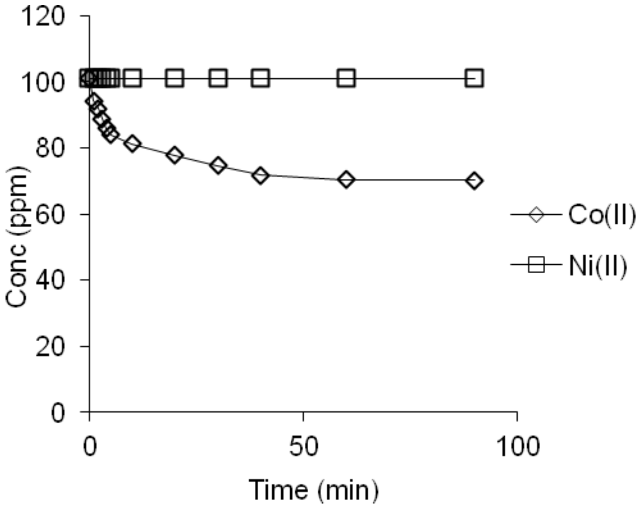

Figure 5.13. Concentration vs. time curves for the selective separation of Co(II) from Ni(II) from a feed solution containing Co(II) and Ni(II) in 2.0M nitric acid

It can be seen in Figure 5.13 that the selective separation of Co(II) can be successfully achieved in 2.0M nitric acid.

5.2.10.2 Selective separation of Ni(II) from Co(II) in 1.0M nitric acid

In Chapter Four it was shown that the maximum extraction of nickel(II) in nitric acid occurred at a concentration of 1.0M nitric acid. Figure 5.14 below shows the extraction curves for a feed solution containing 100ppm Ni(II) and 100ppm Co(II) in 1.0M nitric acid.

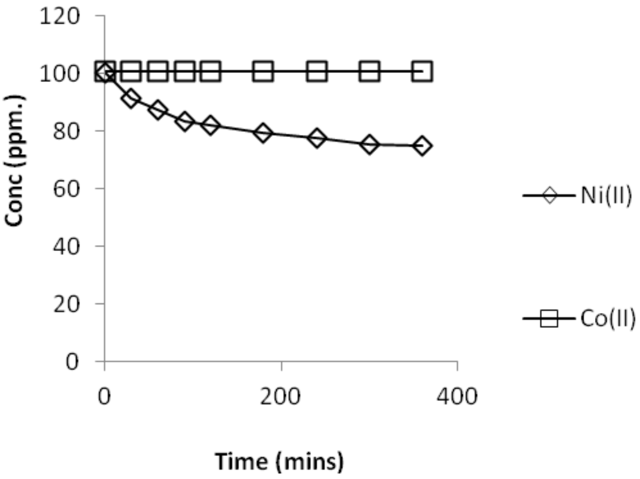

Figure 5.14. Concentration vs. time curves for the selective separation of Ni(II) from Co(II) from a feed solution containing Ni(II) and Co(II) in 1.0M nitric acid

Figure 5.14 shows the extraction curve for the selective separation and extraction of nickel(II) from cobalt(II) in a feed solution that contained 100ppm Ni(II) and 100ppm Co(II) in 1.0M nitric acid.

5.2.10.3 Selective separation of Fe(II) from Co(II) and Ni(II) in nitric acid

In the previous Chapter, it was shown that the optimum extraction of Fe(II) took place in 3.0M nitric acid when a membrane containing 40% (w/w) Aliquat 336/PVC was utilized.

A feed solution that contained 100ppm each of Fe(II), Co(II) and Ni(II) in 3.0M nitric acid was prepared as previously discussed.

The membrane extraction curves that were obtained are shown in Figure 5.15.

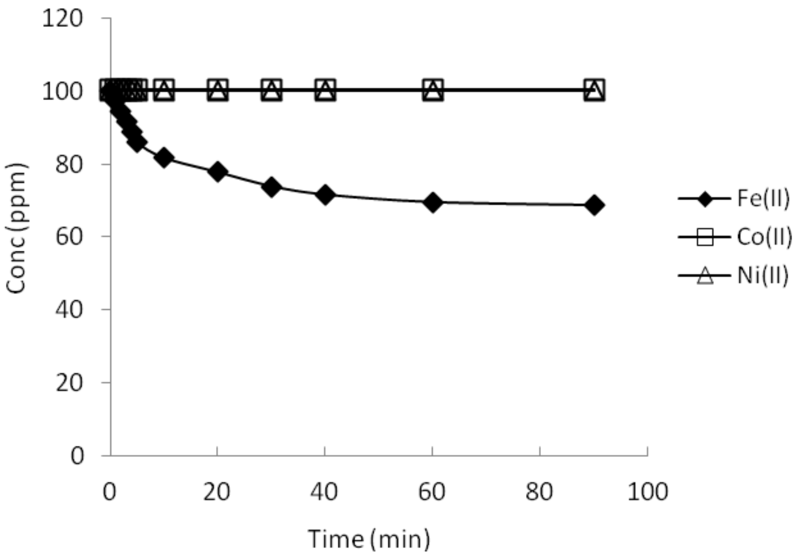

Figure 5.15. Concentration vs. time curves for the selective separation of Fe(II) from Co(II) and Ni(II) from a feed solution containing Fe(II), Co(II) and Ni(II) in 3.0M nitric acid

It can be seen from Figure 5.15 that Fe(II) is extracted whilst both Co(II) and Ni(II) remain in the feed solution.

5.2.10.4 Selective separation of Fe(III) from Co(II) and Ni(II) in nitric acid

In Chapter Four, it was shown that the optimum extraction of Fe(III) took place in 3.0M nitric acid when a membrane containing 40% (w/w) Aliquat 336/PVC was utilized.
A feed solution that contained 100ppm each of Fe(III), Co(II) and Ni(II) in 3.0M nitric acid was prepared as previously discussed.

The membrane extraction curves that were obtained are shown in Figure 5.16.

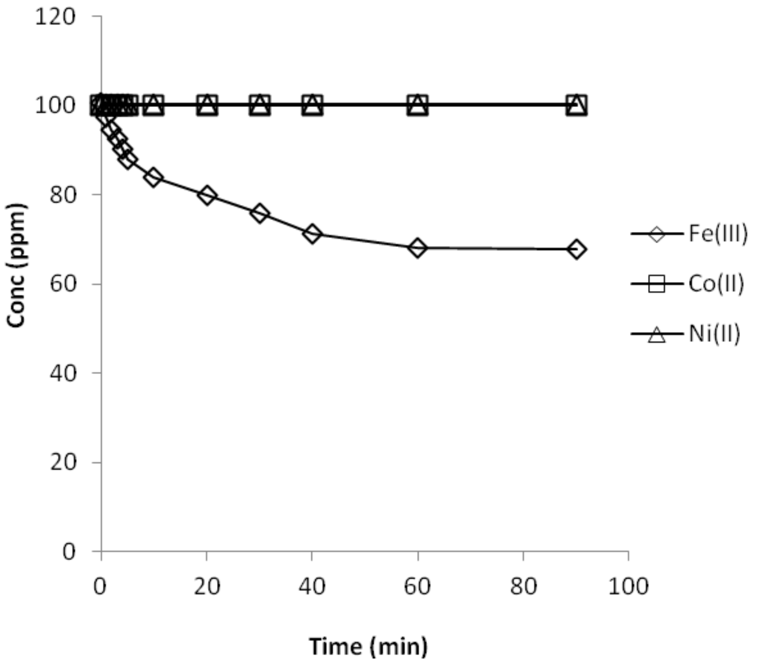

Figure 5.16. Concentration vs. time curves for the selective separation of Fe(III) from Co(II) and Ni(II) from a feed solution containing Fe(III), Co(II) and Ni(II) in 3.0M nitric acid

It can be seen from Figure 5.16 that Fe(III) is extracted whilst both Co(II) and Ni(II) remain in the feed solution.

The selective separation of cobalt(II) from nickel(II) in nitrate solutions containing 2.0M nitric acid and 100ppm Co(II) and 100ppm Ni(II) was achieved using the 40% Aliquat 336/PVC membrane with the changed functional group and it was also shown that the Co(II) could then be completely stripped from the membrane with deionised water with the most likely complex that is formed being $[Co(NO_3)_4]^{2-}$ and it is also reasonable to assume that the same extracted species previously suggested for the extraction are the same as that for the extraction of cobalt(II) in nitric acid that has already been postulated in Chapter Four.

It was also demonstrated that Ni(II) can be selectively separated from Co(II) in 1.0M nitric acid and the nickel(II) can then be completely stripped from the membrane using deionised water with the most likely complex that was formed being

$[Ni(NO_3)_4]^{2-}$. The postulated extracted species of the extraction are most likely that which was already described for the extraction of nickel(II) in nitric acid in Chapter Four.

Other studies showed the selective separation and extraction of both Fe(II) and Fe(III) from Co(II) and Ni(II) in nitric acid with the most likely complexes that were formed being $[Fe(NO_3)_3]^{2-}$ and $[Fe(NO_3)_4]^{-}$ respectively.

5.3 Conclusion

From the studies done for the selective separation and extraction of Co(II) from Ni(II), it can be seen that in 7.0M HCl and using the 40% (w/w) Aliquat 336/PVC membrane, the metals can be selectively separated and extracted using either a two-compartment vessel or a single vessel system irrespective of the initial concentrations of either the Co(II) or the Ni(II) in the feed solution. When other chloride media such as 7.0M lithium chloride, 5.0M potassium chloride, 5.0M sodium chloride and 3.5M calcium chloride are used, the extraction curves follow a similar pattern to that as when Co(II) is extracted on its own. In the conditions that have been described the membrane system shows high selectivity for Co(II) when Ni(II) is added to the feed solution where Co(II) was selectively separated and extracted whilst the Ni(II) remained in the feed solution. The cobalt(II) is completely stripped from the membrane with deionised water. Conversely it was shown that Ni(II) could be selectively separated and extracted from Co(II) in 1.0M hydrochloric acid and other chloride media which included 1.0M lithium chloride, 1.0M potassium chloride, 1.0M sodium chloride and 1.0M calcium chloride.

From the results that were obtained and shown in the extraction curves, it can be deduced that the selective separation and extraction of these metals using the membrane system is dependent on the concentration of the anion in the extraction media. At higher chloride concentrations the membrane system can be used to preferentially extract Co(II) leaving the Ni(II) in the feed solution and at lower concentrations the membrane is selective for Ni(II) whilst the Co(II) remains in the feed solution.

Cobalt(II) was selectively separated and extracted from nickel(II) in 2.0M sulphuric acid and 2.0M nitric acid and the metal could be completely stripped from the membrane using deionised water. Conversely, nickel(II) was selectively separated and extracted from cobalt(II) in 1.0M sulphuric acid and 1.0M nitric acid. The nickel(II) could be completely stripped from the membrane using deionised water. It can be deduced that the concentration of the anion in the feed solution is the main reason for this preferential selectivity of each metal.

For the first time it has been demonstrated that the selective separation and extraction of Co(II) from Ni(II) can be achieved in chloride media, sulphate media and nitrate media using a 40% (w/w) Aliquat 336/PVC membrane where the functional groups matching the media that is used are changed. The Co(II) can then be completely stripped from the membrane using deionised water. It has also been shown that the converse is true when he selective separation and extraction of Ni(II) from Co(II) in chloride, sulphate and nitrate media and back extraction shows that the nickel(II) can be stripped from the membrane in deionised water.

These studies represent the first time that the Aliquat 336/PVC membrane has been shown to be an effective method for the extraction and selective separation and extraction of Co(II) and Ni(II) using chloride media, sulphate media and nitrate media.

The experimental work that has been described also shows the ability of the 40% (w/w) Aliquat 336/PVC membrane system can be used in the selective separation and extraction of three metals that are commonly found together in nature. Both iron(II) and iron(III) were able to be selectively separated and extracted in the presence of cobalt(II) and nickel(II) in 3.0M chloride media,3.0M sulphate media and 3.0M nitrate media. This is the first time that this membrane has been used to definitively achieve such selective separation and extraction, which has been registered under Provisional Patent No 2007900692 titled “Separation of Cobalt, Nickel and Iron in aqueous Solutions", filed in Melbourne, Australia on the 27th August 2004.

It is interesting to note that this simple selective separation system can be easily controlled by the concentration of the anions in the media in the feed solution. This membrane system is an innovative means for the selective separation and extraction for three metals with very similar chemical properties from aqueous solutions.

The amount of metal ion of interest that is to be extracted with the Aliquat 336/PVC membrane is only limited by the number of membranes that are used to achieve the membrane extraction.

The following Chapter will discuss the perceived “gaps” in our understanding of the diffusion process of the membrane and the kinetic processes that are involved where further research would be advantageous for future work.

Chapter Six

Conclusion and Future Work

6.1 Conclusion

The thesis has demonstrated the successful and novel individual extraction of three neighbouring transition metals, cobalt(II),nickel(II) and iron(II) and iron(III) from a variety of aqueous chloride, sulphate, nitrate and oxalate solutions. The work was carried out using an Aliquat 336/PVC membrane and the separation studies demonstrated the conditions for the selective separation of each of these metals from each other in a range of mixed solutions. For the selective extraction of the metal species Co(II), Ni(II), Fe(II) and Fe(III) the concentration of the anion such as chloride has been shown to be the key factor for the metal complex formation with the Aliquat 336. It was postulated that the reason for this was the types of complexes that are formed between the Aliquat 336 and the metal ion and the counter-ion. Previous studies by various researchers show that at various concentrations of the anion a speciation diagram and stability constants of aqueous Co(II) chlorocomplexes at different concentrations of hydrochloric acid can be used to show the most likely Co(II) complex that will be formed. It was earlier established that an anionic metal complex $AuCl_4^-$, in the case of gold, Au(III), was involved in an ion-exchange reaction with Aliquat 336 at the membrane surface to form an ion-pair which then entered the membrane. Based on these previous studies that have also included other metals such as palladium, cadmium and copper, it can be theoretically assumed that a similar pathway is taken for the extraction of other metal ions including those that were studied in this work and that were extracted under similar conditions.

It should also be noted that this is the first time such selective separations and extractions have been carried out using the Aliquat 336/PVC membrane system in a variety of chloride media that included: hydrochloric acid, lithium chloride, potassium chloride, sodium chloride, calcium chloride, suphate and nitrate.

The metal extractions that were done with the changed counter-ion on the Aliquat 336 also highlighted the novel use of the membrane to extend the possible extraction processes in other acidic media apart from chloride. Similarly it was determined that the major factor in the successful extraction of the metal ion complex was found to be dependent on the concentration of the anion present in solution.

Clearly this process has many advantages over the solvent extraction systems that were previously used for the extraction and separation of Co(II), Ni(II) and Fe(III). For example, there is no need for the disposal of toxic, volatile and expensive organic chemicals and solvents that have the potential to cause health issues and environmental damage.

There are several possible applications for the use of this membrane system in the areas of wastewater management. Firstly, the removal of metals from the wastewater of commercial processes such as electroplating, metal finishing and from wastewaters that may contain metal ions in solution that is a result of metal extraction and that needs to be decontaminated before being released or recycled.

Other possible uses could include the purification of drinking water and the removal of toxic metals from rivers and streams which would have environmental benefits for humans and wildlife.

6.2 Future Work

In showing that the extraction and separation of three transition metals with similar chemical properties is able to be achieved on a practical level, it raises the question as to why this is theoretically possible? What other applications can be made using this membrane system and what other factors may be involved in the process apart from the concentration of the anionic species in solution?

It has been previously shown that the extraction of metals using this system is also dependent on the loading of the Aliquat 336, but this does not explain how the diffusion process occurs, and this would be an area for future investigation. Such work would provide a valuable addition to knowledge about how this extraction process occurs and what other variables and factors influence the extraction apart from the concentration of the anionic species in solution. These factors are currently “gaps” in our understanding of this unique process.

The main aim of any future work would be to address the nature of the mechanisms involved in the extraction and the investigation of all the factors that influence the degree to which the ions are separated under different conditions. This could be approached by carrying out kinetic studies of all of the extraction data both for the metals individually and for the extraction and separation processes. Thus this would enable the calculation of equilibrium constants from plots of the data points obtained at the various acid concentrations that were used in the experimental work. This information could then lend weight to the postulation of the mechanism of each metal extracted species in the equilibrium studies.

Further equilibrium studies and kinetic studies of iron(II) and iron(II) would also provide a much better insight into why the ferrous and ferric complexes are able to be extracted under the same conditions and thus lead to a better understanding of the chemistry that is involved in such extractions. Is the ferrous ion oxidized to the ferric ion during the extraction process or is the determining factor the structure if the complex and the hydration shell on the ion a determining factor? A study of the morphology of the complexes that are formed during the extraction process would enhance and help define the postulation of the mechanisms and the chemistry that is involved in the formation of these metal ion complexes.

A long term goal would be to increase the number of metals that can be separated under the conditions that have been demonstrated in this thesis. In particular, other transition metals and a continuing aim is to try to explain why these separations can be achieved with metals that have very similar chemical properties. A comparison of the selectivity and sensitivity on the presence of other cations and anions in the extraction solutions would also yield an area of valuable study.

This investigation has shown the extractability and separation of three transition metals that are alongside each other in the Periodic Table and that possess very similar chemical properties, and this raises the question of whether the elements that sit directly beneath cobalt, nickel and iron such as ruthenium, rhodium and palladium, osmium, iridium and platinum through to the lanthanides, promethium, samarium and europium and the actinides, neptunium, plutonium and americium would also be able to be extracted and separated. If so, why and how this may can take place. Individual extraction studies have already been carried out with palladium [43], and only a few of the other metals have been studied at this point in time. All of the elements suggested share a similar electronic configuration and properties, so it is likely that their extraction and separation may be feasible, although the final actinides would be a hazardous challenge because of their radioactivity.

Finally, there has been limited work done on the morphology of the Aliquat 336/PVC membrane. It has been postulated that the membrane matrix may contain pores or channels within its structure that are responsible for the extraction of metals with the extractant, Aliquat 336. This is an area that requires future investigation and may hold some of the answers as to how the “diffusion” process occurs and the chemistry that may explain this phenomenon.

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