Kinetic Studies on the Extraction of Heavy Metals from Aqueous Stream into Emulsion Liquid Membranes

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CERTIFICATE

This is to certify that the thesis entitled ***"Kinetic Studies on the Extraction of Heavy Metals from Aqueous Stream into Emulsion Liquid Membranes"*** submitted by Mr. Mathurkumar Shambhubhai Bhakhar in fulfillment of the requirements of the Degree of Doctor of Philosophy in Chemical Engineering is a bonafide record of the investigations carried out by him in the Chemical Engineering Department of The Maharaja Sayajirao University of Baroda, Vadodara under my supervision and guidance. In my opinion this thesis has attained the standard fulfilling the requirements of the Degree of Doctor of Philosophy as prescribed in the regulations of university.

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* Research Publications *

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This thesis is dedicated to my parents

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Mathurkumar Bhakhar

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Cc	Carrier concentration, % (v/v)
Ce	Feed concentration at any time t, mg/L
Ceo	Initial feed concentration, mg/L
Cio	Internal phase acid concentration, M
d_{32}	Sauter mean diameter, µm
d_d	Disk diameter, m
d_I	Impeller diameter, m
D_T	Internal diameter, m
H_b	Blade height, m
H_I	Height of the impeller off bottom, m
H_L	Liquid height, m
H_T	Height, m
J	Baffle width, m
L_b	Length of blade, m
N	Speed of agitation, rpm
t	Time, (min. or Sec.)
TR	Treat ratio (dimensionless)
W_{surf}	Surfactant concentration, wt%
β	Separation factor (dimensionless)
ρ	Density, Kg/m^3
γ	Interfacial tension, mN/m
ϕ	Internal phase volume fraction (dimensionless)
μ	Viscosity, cP
SE1	5% (v/v) D2EHPA + 2% (v/v) PC 88A
SE2	5% (v/v) D2EHPA + 2% (v/v) CYANEX 302
SE3	5% (v/v) PC 88A + 2% (v/v) D2EHPA
SE4	5% (v/v) PC 88A + 2% (v/v) CYANEX 302
SE5	5% (v/v) CYANEX 302 + 2% (v/v) D2EHPA
SE6	5% (v/v) CYANEX 302 + 2% (v/v) PC 88A

CHAPTER 1
INTRODUCTION

1.1 General Introduction

Environmental degradation as a result of uncontrolled anthropogenic activity and natural factors has become a major societal issue. An age old problem that has taken frightful dimensions in recent decades is the contamination of water bodies with heavy metal containing wastewater. This poses a potential environmental and insidious health hazard to the living organisms due to the inherent toxicity, coupled with carcinogenicity and mutagenicity associated with these heavy metals. Heavy metals are dangerous because of their tendency of bioaccumulation. Aqueous streams contaminated with heavy metal ions are frequently encountered from various industrial processes such as mining and smelting, electroplating, and metal finishing, fertilizers, rayon, batteries, paint etc. Heightened social awareness makes it imperative for nations, civic bodies, industries, and other organs of civil society to address these problems quickly and consistently. Stringent environmental regulations and growing public awareness, in recent times, have become the major driving force for adopting elaborate treatment technologies for heavy metal loaded wastewaters.

1.2 Background of the work

Several attempts have been made either to treat heavy metal containing effluents for facilitating easy disposal, or to recover the chemicals and recycle the process water. Traditional method of purification such as, distillation, liquid extraction, adsorption and precipitation are still in use; however, the search for competing alternative technologies which may overcome some of the inherent drawbacks of the traditional processes is relentlessly being pursued. Further, most of these processes suffer from the disadvantage of not being necessarily efficient in complete removal of heavy metals from dilute solution when the concentration of solute in the feed stream is ~ 500 mg/L. Removal of heavy metal ions from aqueous solutions has traditionally meant the precipitation of the ion. Such practice is now becoming increasingly unpopular as it produces a sludge leading to a landfill disposal problem. Electrochemical metal recovery is promising; however, waste streams are often dilute in metals and have low plating efficiencies.

Therefore, attempts towards developing membrane-based separation processes to handle wastewater containing heavy metals have assumed paramount importance in recent years.

Common membrane separation processes such as ultra-filtration, dialysis, electrodialysis, reverse osmosis, are widely acknowledged as potentially viable alternative to conventional separation processes such as solvent extraction, distillation, filtration etc. The majority of the membranes used in these processes are solid membranes or membranes supported on solid matrix that tend to foul quickly and also leads to membrane degradation in presence of lixiviants such as ammonia. Separation effected by use of liquid membranes happens to be the latest addition to the list of viable alternatives. The liquid membrane process is a novel and effective method for selective separation and concentration of various species from dilute solutions, including metal ions, weak acids and bases, hydrocarbons or biologically important compounds, and gaseous mixtures.

Conceptually, a liquid membrane can be viewed as a liquid phase that separates two miscible liquid phases across it. Thus, the liquid membrane should be immiscible in the two liquid phases being separated. The type of liquid membrane (either water or oil), therefore will depend upon the type of liquid phases (either oil or water) being separated. If the external phase of an emulsion functions as a liquid membrane an emulsion liquid membrane (ELM) results. Emulsion liquid membranes can offer a number of advantages, these include creation of huge surface area for mass transfer, simultaneous extraction and stripping in a single operation, achieving higher permeate flux, lower capital and operating cost and so on. Additionally, the ELM system can be tailor-made with the great deal of specificity with respect to the process requirement.

1.3 Significance of the work

The increasing demand for heavy metals and the depletion of high quality ores globally make it essential to find effective and efficient methods for the recovery of metal ions even at very low concentration from wastewaters. Liquid membranes are slowly but continuously becoming a very important and promising alternative to the current processing practices normally employed for wastewater treatment, and metals recovery from residual aqueous solutions generated by various industries. Technological functions involve development of the treatment scheme whereby the quantity and concentration of heavy metals is brought within the stipulated safe limits using tailor made emulsion membranes. The form in which the metal is present influences its entry into the food chain and hence, the effort should be to convert to less toxic form.

1.4 Research Objective

There is a considerable interest in the ammoniacal leaching of ores, concentrates, by products and scrap containing metals like copper, nickel, cobalt and zinc. Although extraction of metal from ammoniacal media has been explored by solvent extraction but use of ELM technique for metal extraction from ammoniacal media has not been explored. Therefore a systematic study of extraction of copper, zinc, nickel and their mixtures from ammoniacal solution was desirable.

Extraction of zinc using ELMs has considerable commercial potential and has been investigated by many workers (Draxler, Marr and Protsch 1988, Carvalho and Reis 1993, Carvalho *et al.* 1999, Goto *et al.* 1991, Hoh *et al.* 1982). It has also been commercialized in Austria but numerous irritants remain in the maturing of this technology. There is considerable scope to investigate systematically the effect of different organophosphorous extractants on the efficacy of zinc extraction using ELMs.

The emulsion liquid membrane separation technique by virtue of low energy consumption, high selectivity, speed and efficiency of the process, potential for removing various toxic substances down to very low concentration levels, and easy regeneration of the spent emulsions, have been viewed by researchers as a potentially viable technique for separation of metal ions contaminants from wastewater. In light of the above, the objectives of the present investigation are appended below:

(i) Formulation and characterization of emulsion liquid membrane to study the effect of emulsion composition variables on extraction of heavy metals.

(ii) To study the extraction and stripping behavior of copper and zinc and its mixture from ammoniacal solutions using LIX 84I as extractant.

(iii) To study the effects of various physico-chemical parameters on the ELM extraction of copper, nickel and zinc individually from ammoniacal solutions to set the optimal operating conditions.

(iv) Investigation on co-extraction of copper - nickel mixtures and copper – zinc mixtures from ammoniacal solutions to study the effect of various process parameters and the interaction between metal ions on extraction.

(v) To study the extraction of zinc using different organophosphorous extractants and the underlying synergistic effect of organophosphorous extractant mixtures.

1.5 Outline of the thesis

The thesis is presented in six Chapters, ***Chapter 1: Introduction*** deals with the ideas presented above. ***Chapter 2: Literature Survey*** presents the area of investigation in present context, it highlights the uniqueness and salient aspects of the emulsion liquid membrane technology, it lists the investigation done on metal extraction in the past four decades and also lists the deficiencies of the technology. ***Chapter 3: Materials and Methods*** describes the materials used, experimental technique and analytical techniques adopted in this work and also lists the characterization techniques to bench mark the extractive emulsions. ***Chapter 4: Extraction of heavy metals from ammoniacal solutions*** details our investigation on the extraction of copper, zinc, nickel and the co-extraction of copper and zinc as well as the co-extraction of copper and nickel from ammoniacal media using LIX 84I as the carrier. ***Chapter 5: Extraction of zinc from sulfate solutions*** describes the investigation on extraction of zinc using three organophosphorous extractants as carriers individually as well as in comparison with one another, this chapter also details the synergy observed during the extraction of zinc with mixed extractants. ***Chapter 6: Summary and conclusions*** summarizes the whole investigation and also suggests scope for future work.

CHAPTER 2
LITERATURE SURVEY

2.1 Heavy metals and their environmental impact

The term heavy metal refers to any metallic element having atomic weights between 63.5 and 200.6 with relatively high density of more than ~ 5 gm / cm^3 in their standard state. Heavy metals are further categorized to include *toxic metals* such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc., *precious metals* such as Pd, Pt, Ag, Au, Ru etc. and *radio nuclides* such as U, Th, Ra, Am, etc. Some heavy metals such as Cu, Ni, Cd, Cr, Fe, Zn etc are essential in very low concentrations for the survival of all forms of life while other metals such as Pb, Cd, Hg are toxic also at very low concentrations causing metabolic anomalies, therefore as pointed by Wang and Chen (2006) the boundary between the essential and the toxic effect is somewhat problematic.

Heavy metals are dangerous because of their tendency of bioaccumulation. Compounds tend to accumulate in living things when they are taken up and stored faster than they are metabolized. Bioaccumulation leads to an increase in the concentration of such slowly metabolized chemicals in a biological organism over time compared with the chemical's concentration in the environment Heavy metals mostly enter biological entities from aquatic sources, they can enter a water body from many routes such as industrial and consumer wastewaters, acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater etc.

2.1.1 Source of common heavy metals, their environmental and health hazards

2.1.1.1 Cadmium

Cadmium and cadmium compounds are relatively water soluble compared to other heavy metals. They are therefore also more mobile in soil, generally more bioavailable and tend to bioaccumulate. The source of cadmium in the environment are diverse, some important sources are airborne industrial contaminants, batteries, cigarette smoke, copper refineries, electroplating, fertilizers, food from contaminated soil, fungicides, incineration of tires / rubber / plastic, smelters, soft water, solders (including in food cans), tobacco, vending machine soft drinks, tools, vapor lamps, etc. Cadmium derives its toxicological properties from its chemical similarity to zinc an essential micronutrient for plants, animals and humans.

Cadmium is biopersistent and once absorbed by an organism remains resident for many years although it is eventually excreted. The toxic effects of cadmium on biological systems are reported by various authors Mukherjee *et al.* (1984), Sharma *et al.* (1985). In humans, long-term exposure is associated with renal disfunction and high levels of exposure will result in death. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. The average daily intake for humans is estimated as 0.15 µg from air and 1µg from water. The limiting concentration of cadmium in domestic water is 10 µg / liter. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2 - 4µg of cadmium but levels may vary widely.

2.1.1.2 Chromium

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. Chromium exits in the aquatic environment mainly in two states: Cr (III) and Cr (VI). In general, Cr (VI) is more toxic than Cr (III). Cr (VI) affects human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma (Khezami and Capart 2005).

2.1.1.3 Copper

Copper normally occurs in drinking water from copper pipes as well as from additives designed to control algal growth. Birth control pills, congenital intoxication, copper cookware, copper pipes, industrial emissions, insecticides, bone meal, chocolate, and various food elements such as gelatin, grains, lamb, liver, lobster, margarine, milk, mushrooms, nuts, soybeans, tofu, wheat germ, yeast etc. are also sources for copper. Copper is an essential substance to human life, but the excessive ingestion of copper brings about serious toxicological concerns, such as liver and kidney damage, and stomach and intestinal irritation causing vomiting, cramps, convulsions, or even death (Paulino *et al.* 2006). People with Wilson's disease are at greater risk for health effects from overexposure to copper.

2.1.1.4 *Lead*

Lead in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil and dust from old paint containing lead. Food, air, water and dust / soil are the major potential exposure pathways for infants and young children and non-smoking adult population. In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Lead poisoning, which is so severe as to cause evident illness, is now very rare indeed. At intermediate concentrations, however, there is persuasive evidence that lead can have small, subtle, subclinical effects, particularly on neuropsychological developments in children. Some studies suggest that there may be a loss of up to 2 IQ points for a rise in blood lead levels from 10 to 20 µg / dl in young children. The limiting concentration of lead in domestic water is 50 µg / liter. Lead can cause central nervous system damage. Lead can also damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001).

2.1.1.5 Mercury

Mercury is a global pollutant with complex and unusual chemical and physical properties. The major natural source of mercury is the degassing of the earth’s crust, emissions from volcanoes and evaporation from natural bodies of water. World-wide mining of the metal leads to indirect discharges into the atmosphere. The usage of mercury is widespread in industrial processes and in various products (e.g. batteries, lamps and thermometers). It is also widely used in dentistry as an amalgam for fillings and by the pharmaceutical industry. Concern over mercury in the environment arises from the extremely toxic forms in which mercury can occur. Mercury is a toxic substance which has no known function in human biochemistry or physiology and does not occur naturally in living organisms.

Inorganic mercury poisoning is associated with tremors, gingivitis and/or minor psychological changes, together with spontaneous abortion and congenital malformation. Monomethylmercury causes damage to the brain and the central nervous system, while fontal and postnatal exposure have given rise to abortion, congenital malformation and development changes in young children. Mercury is a neurotoxin that can cause damage to the central nervous system. High concentrations of mercury cause impairment of pulmonary and kidney function, chest pain, dyspnoea (Namasivayam and Kadirvelu, 1999).

2.1.1.6 Nickel

Small amounts of nickel are needed by the human body to produce red blood cells, however in excessive amounts can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems but long-term exposure can cause decreased body weight, heart and liver damage and skin irritation. Nickel can accumulate in aquatic life but its presence is not magnified along food chains. Nickel occurs in environment through butter, fertilizers, food processing, fuel oil combustion, hydrogenated fats and oils, industrial waste, stainless steel cookware, tea, tobacco smoke etc. Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba *et al.* 2006). It is known that nickel is human carcinogen.

2.1.1.7 Selenium

Selenium is needed by humans and other animals in small amounts, but in larger amounts can cause damage to the nervous system, fatigue, and irritability. Selenium accumulates in living tissue, causing high selenium content in fish and other organisms, and causing greater health problems in human over a lifetime of overexposure. These health problems include hair and fingernail loss, damage to kidney and liver tissue, damage to circulatory tissue, and more severe damage to the nervous system.

2.1.1.8 Zinc

Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. Zinc finds its way to the environment through many industrial activities and appears in the form of zinc ash, zinc dross, flue dusts of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge etc. Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyaro *et al.* 2007). The limiting concentration of zinc in domestic water is 5 mg / liter. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Zinc can be a danger to unborn and newborn children. When mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers.

2.1.2 Anthropogenic sources of heavy metal pollution

The major anthropogenic sources of heavy metals from industries and human settlements finding their way into aquatic streams are listed in Table 2.1

Table 2.1: Industrial and domestic source of heavy metal pollution.

Industry	Metals	Source of pollution	Reference
Fertilizers (Agricultural materials)	Cd, Cr, Mo, Pb, U, V, Zn	Run-off, surface and ground water contamination, plant bioaccumulation	Nicholson *et al.* 2003, Otero *et al.* 2005
Batteries	Pb, Sb, Zn, Cd, Ni, Hg	Waste battery fluid, contamination of soil and ground water	EU Directorate general of the environment, 2004
Electronics and electrical	Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn, Ag, Au, Co, Sn, Zn	Aqueous and solid metallic waste from manufacturing and recycling process	Veglio *et al.* 2003, Gray 1999
Metalli-ferous mining	Cd, Cu, Ni, Cr, Co, Zn	Acid mine drainage, tailings, slag heaps	Babich *et al.* 1985
Sewage sludge	Zn, Cu, Ni, Pb, Cd, Cr, As, Hg	Land spreading threat to ground and surface water	Nicholson *et al.* 2003
Specialist alloys and steels	Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn	Manufacture disposal, recycling of metals, tailings and slag heaps	Alloway *et al.* 1993, Rule *et al.* 2006, Cheng 2003
Electroplating	Cr, Ni, Zn, Cu, Fe, suspended material	Liquid effluents from plating processes	Castelblanque *et al.* 2004, Zhao *et al.* 1999, Alvarez *et al.* 2003
Paints & pigments	Pb, Cr, As, Ti, Ba, Zn	Aqueous waste from manufacture, old paint deterioration and soil pollution	Davis *et al.* 1999, Barnes *et al.* 1996, Monken 2000
Rayon industries	Zn	Aqueous wastewater from manufacturing	Jha *et al.* 2007
Tire industries	Pb, Zn, Fe, Cr, Cu, Ni, Al, Mn, Na, K, Ca, Co etc.	Thermal treatment of waste tire fly ash with polyvinyl chloride	Waste recovery Inc., 1986

2.1.3 Major disasters involving heavy metals

***Minamata (1932)**:* Sewage containing mercury was released by Chisso's chemicals works into Minimata Bay in Japan. The mercury was consumed by sea creatures and got accumulated in them leading to mercury poisoning in the local population, consumption of fish polluted with mercury resulted in almost 500 fatalities. Since then, Japan has had the strictest environmental laws in the industrialized world.

Sandoz (1986): Water used to extinguish a major fire carries c. 30 t fungicide containing mercury into the Upper Rhine. Fish were found dead over a stretch of 100 km.

Coto de Donana dam burst ***(1998):*** Dam burst releases 5- million ton of mud containing sulphur, lead, copper, zinc and cadmium in the Coto de Donana nature reserve in southern Spain., Europe's largest bird sanctuary. Experts opine the sanctuary as well as Spain's agriculture and fisheries, will suffer permanent damage from the pollution.

2.2 Assessment of heavy metal removal techniques from aqueous streams

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence poses disposal problems due to their non-degradable and persistent nature. In addition mining, mineral processing and extractive-metallurgical operations also generate toxic liquid wastes containing heavy metals. Faced with ever stringent regulations, heavy metals are now environmental priority pollutants which, need to be removed from the wastewaters to protect the human ecosphere. Various techniques that are being used to remove heavy metal ions include ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, chemical precipitation, chemical oxidation or reduction, reverse osmosis etc. These processes may be ineffective or extremely expensive especially when the metals in solution are in the concentration range of 1–100 mg / 1iter (Nourbakhsh *et al.* 1994).

2.2.1 Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. Various adsorbents have been tried out for heavy metal recovery. Activated carbon adsorbents are widely used in the removal of heavy metal contaminants because of their high surface area. In recent years there has been considerable amount of interest in the utilization of carbon nanotubes for removing heavy metal ions such as lead (Wang *et al.* 2007a, Kabbashi *et al.* 2009), nickel (Kandah and Meunier 2007), cadmium (Kuo and Lin 2009), chromium (Pillay *et al.* 2009), copper (Li *et al.* 2010), from wastewater. Jusoh *et al.* (2007) and Kang *et al.*

(2008) have reviewed the current work done in this field. However, carbon nanotubes as adsorbents suffer from the disadvantage of being very expensive.

The main focus of investigations in the past decade has been to search for a low cost effective adsorbent. Till date hundreds of studies on the use of low-cost adsorbents have been published (Fu and Wang 2011). Agricultural wastes, industrial byproducts and wastes, bioadsorbents and other natural substances have been studied as adsorbents for the heavy metal wastewater treatment. Several reviews by Babel and Kurniawan (2003), Sud *et al.* (2008), Wan and Hanafiah (2008), Apiratikul and Pavasant (2008b), Bhattacharyya and Gupta (2008) are available that discuss the use of low-cost adsorbents for the treatment of heavy metals wastewater. In spite of extensive research focus, a cheap adsorbent alternate to activated carbon has yet not been identified. It is likely that activated carbon will remain the work horse for many years to come.

2.2.2 Chemical precipitation

Precipitation is the most commonly used method for removing toxic heavy metals up to parts per million (ppm) levels from water because it is relatively simple and inexpensive to operate (Ku and Jung 2001).

Table 2.2: Recent work on chemical precipitation of heavy metals

Species	Initial metal conc.	Precipitant	Optim. pH	(%) Removal	References
Zn(II)	32 mg/L	CaO	9-10	99-99.3	Ghosh *et al.* 2011
Cu(II), Zn(II), Cr(III), Pb(II)	100 mg/L	CaO	7-11	99.37-99.6	Chen *et al.* 2009b
Cu(II), Zn(II), Pb(II)	0.018, 1.34, 2.3 mM	H_2S	3.0	100, >94 and >92	Alvarez *et al.* 2007
Cr(III)	5363 mg/L	CaO and MgO	8.0	>99	Guo *et al.* 2006
Hg(II)	65.6, 188 mg/L	1,3- benzenediamidoethanethiolate	4.7 and 6.4	>99.9	Blue *et al.* 2008
Cu(II) - EDTA	25, 50, 100 mg/L	1,3,5-hexahydrotriazinedithiocarbamate	3.0	>99	Fu *et al.* 2007

The conventional chemical precipitation includes hydroxide and sulfide precipitation. Its efficiency is affected by low pH and the presence of other salts. The process requires addition of other chemicals and results in the production of a high water content sludge that could be toxic and poses huge disposal problems that are expensive as well (Gray 1999). Table 2.2 lists some of the recent work carried out by various investigators on chemical precipitation of heavy metals.

Cementation is a type of precipitation method in which a metal having a higher oxidation potential passes into solution to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au. Heavy metals such as Pb, As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.

2.2.3 Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum, ferrous sulphate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates.

El Samrani *et al.* (2008) investigated the removal of heavy metal by coagulation using two commercial coagulants, a ferric chloride solution and a poly-aluminum chloride (PAC). They found excellent heavy metal elimination was achieved within a narrow range of coagulant around optimum coagulant concentrations. Coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles.

Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form (Shafaei *et al.* 2010, Kabdash *et al.* 2009, Parga *et al.* 2005, Olmez 2009).

2.2.4 Electrochemical treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and expensive electricity supply, so they have not been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Wang *et al.* 2007b).

Electroflotation (EF) is a solid/liquid separation process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. The application of the optimized parameters on the separation of some heavy metal ions such as iron, nickel, copper, zinc, lead and cadmium was studied and demonstrated that the metal removal rate reached 99%. The treatment of wastewater using the EF technique with aluminum electrodes was studied by Belkacem *et al.* (2008).

Oztekin and Yazicigil (2006) investigated the electrolytic recovery of metals from aqueous solutions containing complexing chelating agents such as EDTA, nitrilotriacetic acid and citrate in a two-chamber cell separating with a commercial cation exchange membrane. Their results showed that least value of recovery of metal was approximately 40% and it increased up to 90% for copper by optimizing experimental conditions. Chang *et al.* (2009a) used electrodeposition in conjunction with ultrasound to reclaim EDTA-copper wastewater. They found that the technique can effectively remove copper (95.6%) and decompose EDTA (84% COD removal) from wastewater.

Electro-winning is widely used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes (Gray 1999).

2.2.5 Flotation

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. Dissolved air flotation involves generation of micro-bubbles of air that attach to the suspended particles in water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge (Lundh *et al.* 2000). Dissolved air flotation had been widely studied to remove heavy metal in 1990s (Waters, 1990; Tassel *et al.* 1997, Tessele *et al.* 1998).

Ion flotation has been shown a promising method for the removal of heavy metal ions from wastewaters. The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles (Polat and Erdogan 2007). Yuan *et al.* (2008) investigated the potential of ion flotation to remove cadmium, lead and copper from dilute aqueous solution with a plant-derived biosurfactant tea saponin. Hexadecyltrimethyl ammonium bromide was used as collector. Ethanol and methyl isobutyl carbinol were used as frothers. Metal removal reached about 74% under optimum conditions at low pH. At basic pH it became as high as 90%, probably due to the contribution from the flotation of metal precipitates. Precipitate flotation process is another alternative of flotation method, based on the formation of precipitate and subsequent removal by attachment to air bubbles. Capponi *et al.* (2006) have indicated that depending on the concentration of the metal solution, the precipitation may proceed via metal hydroxide formation or as a salt with a specific anion such as sulfide, carbonate, etc.

2.2.6 Ion exchange

Ion-exchange has been widely used to remove heavy metals from wastewater due to their varying advantages, such as high treatment capacity, high removal efficiency and fast kinetics. Though it is relatively expensive when compared with other methods, it has the ability to achieve ppb levels of clean up while handling relatively large volumes of feed (Kang *et al.* 2004).

Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Synthetic resins are commonly preferred since they are effective to nearly remove the heavy metals from the solution (Alyuz and Veli 2009).

The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution (Ahluwalia and Goyal 2007).

2.2.7 Membrane technologies

Membrane technologies with different types of membranes show great promise for heavy metal removal due to their high efficiency, easy operation and space saving. Membrane processes used to remove metals from the wastewater are ultrafiltration, reverse osmosis, nanofiltration and electrodialysis.

Table 2.3: Recent investigations on heavy metal ion removal using membrane techniques

Membrane	Heavy metal	Initial metal Conc.	Removal efficiency	Conditions	References
RO	Cu(II) Ni(II)	500 mg/L	99.5	Operation pressure 5 atm	Mohsen-Nia *et al.* 2007
RO	Cu(II)	20-100 mg/L	70 - 95	Low pressure reverse osmosis combined with electro winning	Zhang *et al.* 2009
RO	As(III) As(V)	< 500 mg/L	As(V) 91-99, As(III) 20-55	NA	Chan *et al.* 2008
RO	Ni(II), Zn(II)	44-169 mg/L 64-170 mg/L	99.3 98.9	Operational pressure 1100 kPa	Ipek, 2005
NF	Cu(II)	10 mM	47-66	Transmembrane pressure (1-3 bar)	Chaabane *et al.* 2006
NF	Cr(VI)	NA	99.5	Surfactants enhanced NF	Muthukrishnan *et al.* 2008
NF	Cu(II)	0.47 M	96-98	Flat sheet NF membranes at 20 bar	Tanninen *et al.* 2006
RO + NF	Cu(II)	2 g/L	>95	Operating pressures 35 bar	Csefalvay *et al.* 2009
RO + NF	Cu(II)	15 mg/L	95-99	Combination of flotation and membrane filtration, 3.8 bar	Sudilovskiy *et al.* 2008

Ultrafiltration has been the most popular membrane technique for heavy metal recovery. To enhance removal efficiency of metal ions; variants such as micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) were proposed as reviewed by Fu and Wang (2011). Recently nanofiltration has been gaining ground particularly for the removal of arsenic by Erikson (1988), Figoli *et al.* (2010), nickel by Murthy and Chaudhari (2008) and Cu by Csefalvay *et al.* (2009), Ahmad and Ooi (2010). Table 2.3 provides a summary of some of the recent investigations on selected heavy metal removal using membrane techniques.

Table 2.4 shows the advantages and disadvantages of the various treatment technologies for removal of heavy metals from wastewater using conventional separation processes.

Table 2.4: Advantages and disadvantages of the various treatment technologies

Technology	Advantages	Disadvantages	References
Adsorption	Wide variety of metals ions and pollutants, high capacity, fast kinetics possibly selective depending on adsorbent.	Performance depends on type of adsorbent, chemically reactivation to improve it adsorption capacity.	Crini, 2005
Chemical precipitation	Process simplicity, not metal selective, inexpensive capital cost.	Large amount of sludge containing metals, sludge disposal cost, high maintenance costs.	Aderhold *et al.* 1996
Coagulation–flocculation	Bacterial inactivation capability, good sludge settling and dewatering characteristic.	Chemical consumption, increased sludge volume generation.	Aderhold *et al.* 1996
Electro-chemical treatments	No chemical required, design to tolerate suspended solids, moderately metal selective effluent treatment for particle density > 2000 mg/ liter.	High initial capital cost, production H_2 with some of the processes, required filtration process for flock.	Kongsrich-aroern *et al.* 1995, 1996
Flotation	Metal selective, Low retention times, removal of small particles.	High initial capital cost, High maintenance and operation costs.	Rubio *et al.* 2002
Ion-exchange	Metal selective, limited pH tolerance and high regeneration.	High initial capital cost, High maintenance costs.	Aderhold *et al.* 1996
Membrane filtration	Low solid waste generation, low chemical consumption, small space requirement possible to be metal selective.	High initial capital cost, high maintenance and operation costs, membrane fouling, limited flow-rates.	Madaeni *et al.* 2003, Qin *et al.* 2002

2.3 Emulsion liquid membrane separations

2.3.1 Background

A membrane is defined as a semi-permeable barrier between two miscible fluid phases it selectively allows passage of some components across it while restricting the passage of other components. When a liquid serves as a barrier between two phases it is called as a liquid membrane. Different solutes have different solubilities and diffusion coefficients in a liquid hence the extent and rate of transport of different solutes vary across the liquid membrane due to this, liquid membranes are also known as solubility membranes. Since the diffusion coefficients in liquids are typically orders of magnitude higher than in polymers hence a large flux is observed in liquid membranes compared to solid polymeric membranes.

Emulsions are dispersions of two liquid phases immiscible with each other stabilized by using an appropriate surfactant called emulsifier, emulsions are of two types

- Water in Oil (W/O) emulsions, when the external continuous phase is the oil phase in which the water phase is dispersed.
- Oil in Water (O/W) type where water is the continuous phase and the oil phase is dispersed in it.

A W/O emulsion can be dispersed in a continuous phase of water because the oil phase of the emulsion will prevent the two water phases- *the internal water phase of the emulsion and the continuous water phase in which the emulsion is dispersed*, from homogenizing with each other. Thus the oil phase of the emulsion acts as a membrane in a system involving a W/O emulsion dispersed in water. Similarly in an O/W emulsion dispersed in oil the water phase as the liquid membrane.

The emulsion liquid membrane separation technique was invented by Li (1968) in the Exxon laboratories, who initially used O/W emulsion to separate paraffin's from aromatics but, it was quickly realized that ELMs would be a far better tool to separate solutes from aqueous streams using W/O emulsions, subsequently Li and coworkers (Li and Frankenfeld 1988, Li and Shrier 1972, Chan and Li 1974, Matulevicius and Li 1975, Halwachs, Flaschel and Schugerl 1980, Noble, Way and Bunge 1988, Marr, Bart and Draxler 1990, Ho 1990) separated toxic substances such as phenols and heavy metals from water into ELMs.

2.3.2 Emulsion liquid membrane separation (ELMs) process for solute removal from aqueous feed streams

Emulsion liquid membranes (ELM) for removal of solutes from aqueous streams are formed by preparing a W/O emulsion and then dispersing the same in a continuous aqueous feed that needs to be treated. The emulsion is prepared by mixing known volume of oil phase with a suitable emulsifier having HLB (hydrophile lipophile balance) value ranging from 6 to 8 to produce the chosen emulsion. To this oil phase known volume of aqueous phase containing the selected stripping reagent is added. The resulting oil-water mixture is then intensely agitated using a high speed mixer or in a high pressure homogenizer to give the W/O emulsion.

The resulting milky white emulsion is then dispersed in the continuous water phase with mild agitation. The emulsion breaks up into tiny globules of ~ 2 mm size and within each globule there exists multitude of tiny droplets of the internal aqueous phase having size usually in the range of 0.2 to 10 μm. The large surface area generated in this process leads to very rapid rates of removal of pollutants/solutes of interest from the feed phase. After a certain specified time of contact between the emulsion and the feed phase the agitation is stopped this leads to the separation of the emulsion phase from the denser feed phase. The two phases can then be separated by decantation. Contact with the emulsion leads to the removal of the solute from the feed phase and its concentration in the emulsion phase. A schematic of the ELM process is shown in Fig 2.1

The W/O emulsion is subsequently destabilized so that it breaks up in to its constituents the oil phase which constitutes the membrane phase is appropriately recycled while the internal aqueous phase containing the desired solute is taken up for suitable processing such as electro winning of metals. The effectiveness of the ELM separation technique largely depends on the capacity of the emulsion to load solutes. It was Li who visualized that the capacity of ELM for removal of solutes such as phenols would be restricted if the inner phase of the emulsions do not contain a suitable reactive reagent, while in the presence of an appropriate reactive reagent the capacity of the process could be substantially enhanced.

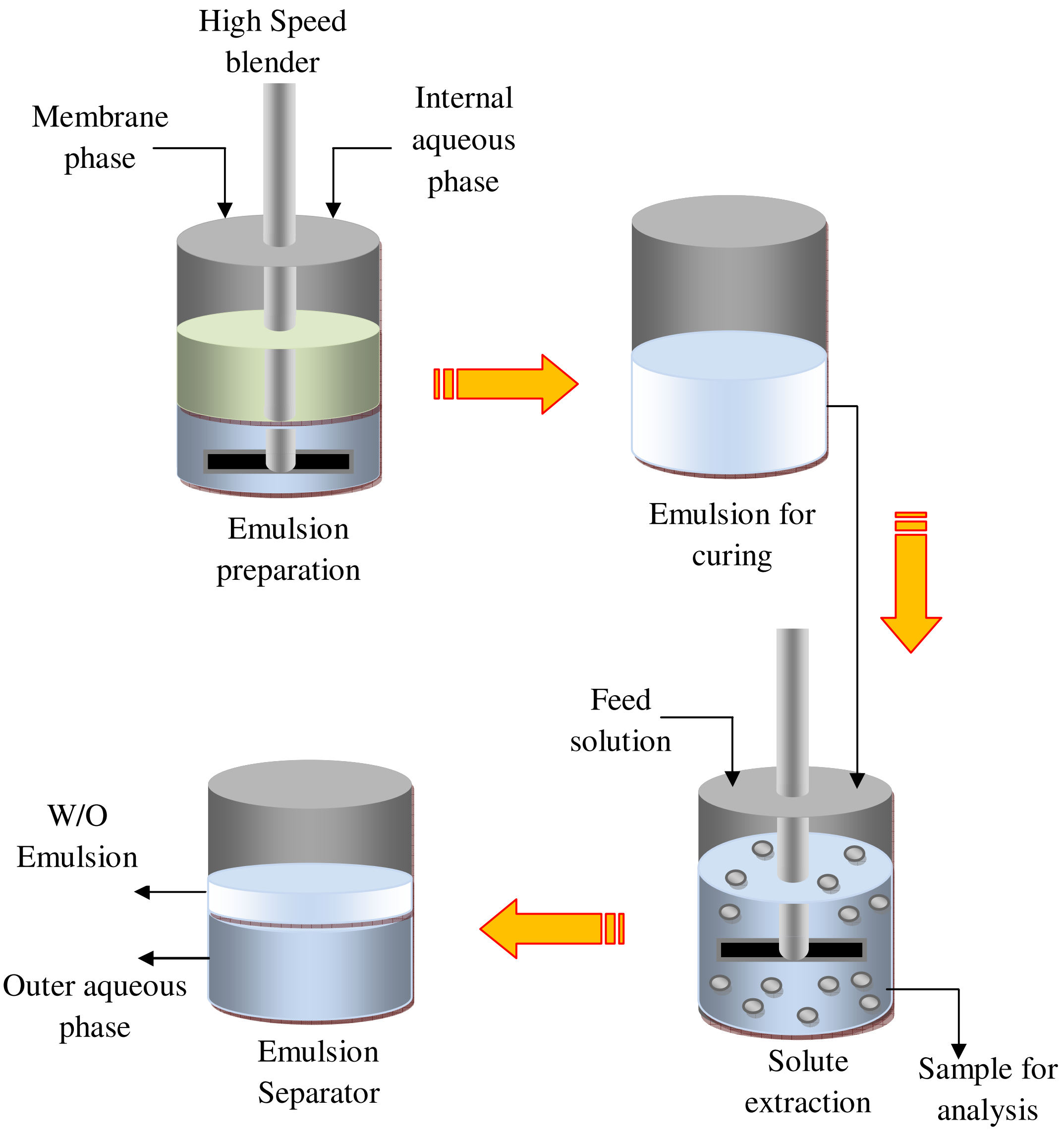

Fig. 2.1 Schematic of the ELM process

Thus for the case of phenol removal from bulk solutions using an emulsion liquid membrane would not yield any significant removal if the inner phase of the ELM consists of only water. The extraction would stop when the concentration of phenol becomes identical in the internal phase of the ELM and external aqueous phase, which would contribute to a small amount of phenol being extracted. However if a reagent such as NaOH is present in the internal phase then the phenol transferred in the internal phase would react instantaneously as per reaction 2.1.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O \qquad \ldots\ldots (2.1)$$

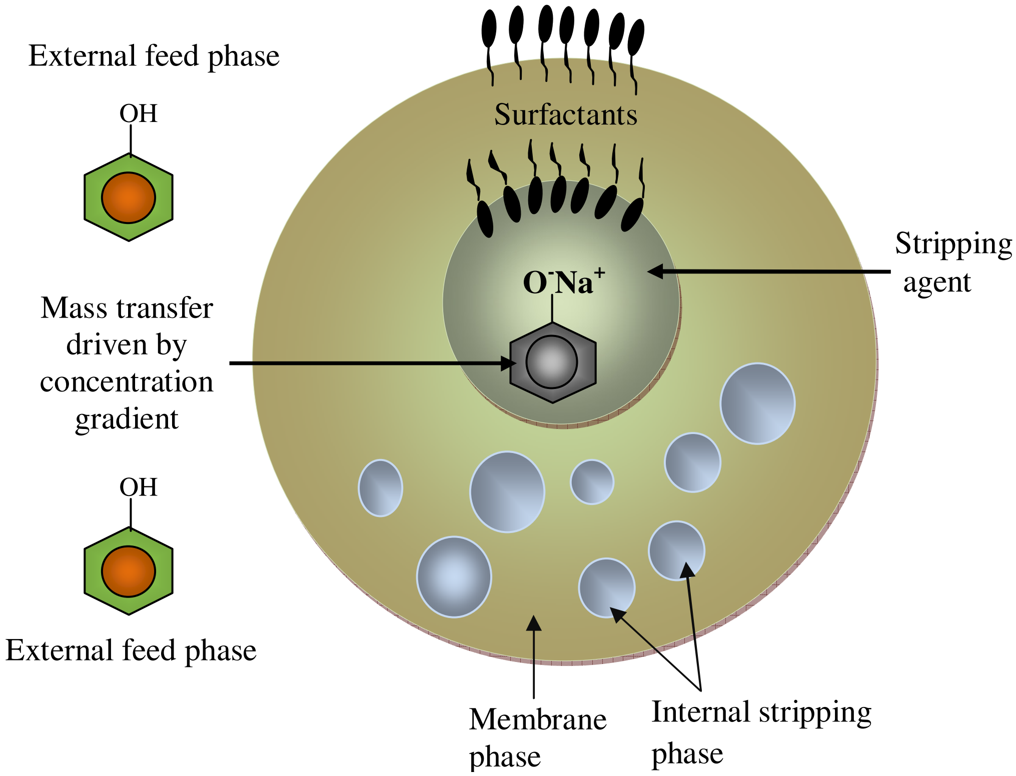

Fig. 2.2 Schematic of phenol extraction by ELMs

As long as NaOH concentration exists in the inner phase the reaction continues, thus NaOH serves three purpose:-

i. It enhances the capacity of the emulsion to load the solute.

ii. It maintains concentration gradient for phenol to diffuse in the emulsion resulting in enhanced transport rates.

iii. It entraps the solute in the internal aqueous phase of the emulsion and does not permit the back diffusion of the species because while phenol is oil soluble, sodium phenolate is not.

The cumulative effect is rapid rates of extraction of phenol from the bulk phase is shown in Fig. 2.2. Such transport mechanism in ELM systems wherein the solute penetrates within the membrane by virtue of its concentration gradient is called as ***Type I transport mechanism***. Some typical examples of Type I transport are removal of phenols, organic acids, ammonia, amines, urea etc.

In case of metals ions because of their insolubility in oil phase, it becomes necessary to incorporate a metal extractant in the oil membrane phase to facilitate the transport. The metal ion binds with the extractant to form an extractant- metal complex at the feed – emulsion interface often called the external interface in ELM literature. The extractant – metal complex formed transfers the metal ion in the oil membrane phase in which the complex is usually highly soluble.

The metal complex then diffuses away from the external interface to the inner space of the emulsion globules due to the concentration driving force. In its journey within the globule the metal complex arrives at the inner oil-water interface where the metal ion gets stripped from the extractant by reaction with a suitable stripping agent as shown pictorially in Fig 2.3. The metal ion is released and encapsulated within the internal droplets of the emulsion globule, rendering the extractant molecule free to diffuse back to external interface to bind and transport more metal ions to the inner droplets within the emulsion globule. This process continues till the internal stripping phase is not totally exhausted. Since the extractant molecule functions as a carrier it is called so in ELM literature. Such carrier mediated transport is also known as ***Type II facilitated transport mechanism***. Transport of metal ions as well as biochemicals such as tryptophan, L-Leucine, penicillin G etc are examples of carrier mediated transport.

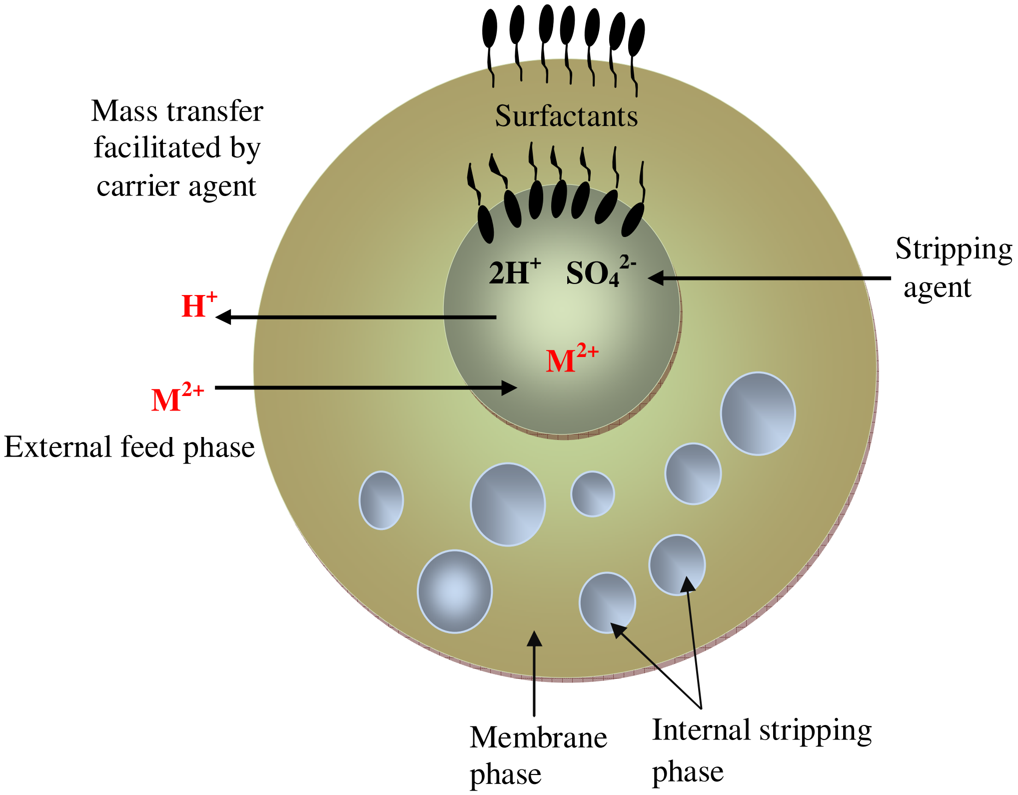

Fig. 2.3 Schematic of metal ion extraction by ELMs

Emulsion liquid membrane separations offer the following advantages over other conventional separation techniques.

- High flux is achieved and rapid extraction with relatively high efficiency due to large internal droplet surface area of the ELM (10^6 m^2/m^3) available for mass transfer. The selective nature of the carrier provides much better separations than those obtained solely from differences in the permeability coefficient.

- System can be tailor made with great deal of specificity, lower capital as well as operating cost and low energy consumption especially compared to other separation processes such as thermal evaporation, electrodialysis and pressure-driven membrane processes.

- Potential for removing various toxic substances down to very low concentration levels and ions can be concentrated since the coupled transport mechanism can pump one ion against its concentration gradient due to a gradient in the coupled ion.

- Particularly in emulsion type of liquid membrane extraction and stripping of species can be achieved simultaneously. Separation can be highly selective when carrier agents are used in the membrane phase that binds exclusively with target compounds; possibility of achieving high separation factor and possibility of concentrating recovered species during the separation operation itself. Expensive complexing agents are required in small amounts.

- Easy regeneration of the spent emulsions using a demulsification process.

2.3.3 Emulsion liquid membrane formulation for metal extraction

The use of liquid membranes containing carriers has been proposed as an alternative to solvent extraction processes for the selective separation, purification and concentration of metal ions in aqueous solutions, organic acids, bio products and gases. Emulsion liquid membranes can be “tailor made” to meet the requirements of different separations, and thus they offer versatile process capability for separating a wide range of heavy metal ions from solutions. However, for type II facilitation, an extractant and its associated stripping agent must be incorporated into the membrane and internal phases, respectively, in order to achieve a coupled extraction / stripping and regeneration operations in a single stage.

The essential components of an ELM system for metal extraction are the organic diluent, emulsifier, carrier and the stripping agent. Of these four components the first three make up the membrane phase while the stripping agent usually water soluble finds its place in the internal phase of the membrane.

2.3.3.1 Membrane material

The major constituent of the membrane phase is a aliphatic and aromatic solvent. It is critical to employ an appropriate solvent as membrane phase for an efficient ELM process. There are several considerations in choosing a suitable solvent as pointed by Ho and Sirkar (1992)

i. low solubility in the external feed phase and the internal stripping phase in order not to lose the solvent during emulsion preparation and solute extraction,

ii. compatibility with dissolved surfactant and extractant,

iii. moderate viscosity balancing the membrane stability and permeability,

iv. enough density difference from the aqueous phase for the fast process of emulsion separation,

v. low cost of its production,

vi. low toxicity because of environmental concern.

Considering the above criteria of the membrane phase, aliphatic solvents are preferred over aromatic solvents since they meet most of the above requirements. Membrane materials used to formulate the emulsion liquid membranes could be classified in the following four categories:-

- Proprietary solvents: These include Exxon's S100 N® a dewaxed isoparaffinic middle distillate (M.Wt 386.5 and specific gravity of 0.85 at 25°C), Exxon's LOPS® 'Low odor paraffin solvent' containing 52% Paraffin, 45% napthenes and 3% aromatics, Shellsol T® paraffinic solvent from Shell containing less than 0.5% aromatics. Almost all the early work on ELM technology done by Li and coworkers (Terry, Li and Ho 1982, Downs and Li 1981, Li, Cahn and Shrier 1973), Marr and coworkers (Draxler and Marr 1986, Draxler, Furst and Marr 1988, Marr, Bart and Draxler 1990) were done using these solvents.

- Petroleum fractions: These include kerosene and liquid paraffin. Currently, kerosene has emerged as the most popular membrane material.
- Pure solvents: Solvents such as n-heptane, n-dodecane, o-xylene, toluene etc. have been used by some investigators.
- Mixed solvents: Kerosene – liquid paraffin mixtures, kerosene-heptane, kerosene-xylene blends have been used. The rationale of using mixed solvents is to get a membrane phase with enhanced aliphatic content.

The various membrane materials used by different investigators for metal extraction are listed in Table 2.5.

2.3.3.2 Emulsifier

A reasonably stable emulsion is the key for the success of an ELM process. Emulsions are thermodynamically unstable hence an emulsifier has to be added to the oil phase of an W/O emulsion to ensure stability of the emulsion. Using appropriate type and amount of the emulsifier emulsion stability can be modulated and thus ensured for the duration of the process. The emulsifier also affects several other parameters such as osmosis, water solubility, and mass transfer resistance (Draxler and Marr 1986). The emulsifying agents form an interfacial film around the dispersed internal droplets and this film prevents or retards the droplets from coagulation and flocculation (Cavallo and Chang 1990).

Very limited attempts have been made to design emulsifiers for ELM applications. The most widely used emulsifier for preparing W/O emulsions for ELM applications is sorbitan monooleate (Span 80$^{®}$ having a molecular weight of 428). The popularity of Span 80 as an emulsifying agent stems from the following reasons: It provides relatively stable emulsions that are easily demulsified and it shows less resistance to mass transfer in comparison with other emulsifiers (Draxler and Marr 1986, Draxler *et al.* 1988, Nakashio *et al.* 1988, Strzelbicki and Schlosser 1989, Lee and Chan 1990). However it suffers from some drawbacks, emulsions prepared from Span 80 are prone to osmotic swelling (Martin and Davies 1977, Colinart *et al.* 1984, Hirato *et al.* 1990, Abou-Nemeh and van Peteghem 1990). Emulsions prepared with Span 80 are not very stable under highly alkaline conditions due to hydrolysis of ester linkages of the emulsifier (Abou-Nemeh *et al.* 1990, 1992, 1993).

Nonionic polyamine surfactant ECA 4360 (MWt = 1800) and its derivatives are reported to form more stable emulsions compared to Span 80 (Goto *et al.* 1987), cause less osmotic swelling (Nakashio *et al.* 1988) and are sparingly soluble in water (Draxler, Furst and Marr 1988). However, this emulsifier shows poor stability with organic and inorganic acids (Draxler and Marr 1986). ECA 4360 also suffers from the drawback of providing high resistance to interfacial mass transfer (Wasan, Gu and Li 1984). Some emulsifiers have synergistic effect with carriers. Miyake *et al.* (1983) observed that the extraction rate with carrier SME 529 was accelerated by anionic surfactants. Zhang *et al.* (1989, 1990) observed that polyamine surfactant N 205 enhanced the extraction of rare earths.

Gu, Ho and Li (1992) attribute the following properties desired from an emulsifier. It should be soluble in the membrane phase only and not in the internal stripping phase or the external feed phase in order not to lose any surfactant during operation. It should not react with the carrier in the membrane phase, it must have a low interfacial resistance to mass transfer and should be stable against acids, bases, and bacterial activity. Lastly it should not inhibit demulsification. In addition it should be cheap, easily available, non toxic and environmental friendly. However, there is no single emulsifier that satisfies all these attributes. Mostly investigators and process engineers choose from what is available at a reasonable cost, but the quest for synthesizing an ideal emulsifier for specific applications continues.

2.3.3.3 Carrier

Carrier is the most important ELM component in type II facilitated transport. The role of carrier is not only to facilitate the separation but also to enhance the separation selectivity. Further the selection of the stripping agent is coterminous with the choice of the carrier. Selection of the carrier (metal extractant) and stripping agents requires considerable chemical insight. When choosing a carrier, one needs to keep in mind that the selected extractant and its complex must be soluble in the membrane phase, but insoluble in the external and internal phases. Moreover, precipitates should not form either within the membrane or at the interfaces (Cussler and Evans 1974).

Generally, the selection of extractant / stripping agent system is based on the thermodynamic and kinetics considerations. Thermodynamically, the selected extractant should favor the distribution of the solute from the external phase to the membrane phase. On the contrary, a stripping agent must be thus selected to partition the solute from the membrane phase to the internal phase. A thermodynamic condition exists under which the liquid membrane process can be operated while solvent extraction cannot. A solvent extraction process needs a high distribution ratio for extractant so as to increase the extraction ability. The non-equilibrium feature of emulsion liquid membranes allows the selected extractant to have lower distribution ratio for extraction than solvent extraction. For instance, an extractant, which has a low distribution ratio for Cr(VI) extraction and thus is unsuitable for a solvent extraction process, was successfully used as carrier to separate Cr(VI) in an ELM systems by Yan *et al.* (1990a).

Kinetically, the selected extractant and stripping agent should usually exhibit fast reactions for both extraction and stripping. But it is interesting to note that because of its much higher interfacial area for stripping than that for extraction, an emulsion liquid membrane is capable of coping with the situation in which the extractant has relatively fast extraction kinetics but the stripping agent offers slow stripping kinetics. Draxler and Marr (1986) observed that although DTPA and Cyanex 301 are very strong extractants for metal ions but they are nearly unknown in solvent extraction due to the extremely slow stripping kinetics of extractants. However, they used these extractants to concentrate Zn(II) and Ni(II) effectively in ELMs.

For the recovery and purification of metals from aqueous leach solutions by solvent extraction using a metal extractant, Sudderth *et al.* (1986) recommend the following criteria be met by the extractant, it also serves as a pointer for what is expected of a carrier in an ELM process for metal extraction:-

- The extractant must be soluble, both in its loaded and stripped form, in relatively inexpensive diluents which also meets the environmental and workplace regulations.
- The extractant must be chemically and physically stable in the solvent extraction circuit so that it can be recycled through extraction and strip many times without experiencing undue physical loss or chemical breakdown.
- The reagent must meet today’s stringent environmental and work place regulations
- The extractant should be able to be stripped to produce a solution from which the desired metal can be recovered in an acceptable form. The metal may be recovered in a number of forms including electrowon cathode, crystallized salts, or precipitated salts.
- The extraction and strip kinetics must be sufficiently fast to allow these processes to take place in an industrially acceptable time frame.

- Phase separation between the organic and feed / strip phase should be rapid with minimum level of entrainment.
- The extractant must not transfer deleterious species back from the strip section to the extraction section.
- The extractant should be tolerant of crud and should not promote crud formation
- The extractant must have a reasonable cost, which will enable it to provide an economically attractive recovery route for the metal being treated.

Meeting these criteria to an acceptable level imposes great restrictions on the number of chemicals which have found commercial use as extractants. While there are many hundreds of reagents which have been developed and tested in the laboratory but very few of these have found commercial acceptance.

The combination of restraints imposed by the properties of the metals and the required properties of the reagents used to extract them has limited the number of metals recovered in significant quantities by solvent extraction techniques. Despite these limitations almost 25% of the worlds copper and most of the world's uranium is recovered this way. Solvent extraction is becoming much more widespread in the recovery of nickel from lateritic ores and has long been used in nickel refining from chloride leach solutions. Precious metals, rare earths, and pollutants such as arsenic are also recovered by solvent extraction. Although direct correspondence between solvent extraction of metals and ELM extraction of metals may not be possible in all cases because while solvent extraction is equilibrium limited process, ELM extraction is primarily rate limited process. Nevertheless the knowledge of extraction behavior of extractants for various metal species can be effectively transported across the techniques.

Extractants in general are grouped into three classes by Gu *et al.* (1988) according to the functional groups:

- acidic extractants
- basic extractants,
- neutral extractants

Acidic extractants and their associated stripping agents

To extract a cation from an aqueous solution, it must be combined with an anionic species to form an uncharged species. Acidic extractants are most effective for extraction of cations by exchanging their protons for the cations for liquid membrane cation extraction. Commonly used acidic extractants can be classified into three groups.

1) Chelating extractants, which include (a) hydroxyoximes marketed as LIX reagents by Cognis Inc. such as LIX 63, LIX 64N, LIX 65N, LIX 70, LIX 84, Shell SME 529, Acoroga reagents P17, P50, and PT5050 etc (b) β-hydroxyquinolines (oximes) such as Kelex 100; and (c) β-diketones such as acetylacetone and benzoylacetone.

2) Alkylphosphorous compounds, which include (a) organophosphoric acid such as di(2-ethylhexyl)phosphoric acid D2EHPA, and dibutylphosphoric acid (DBP); (b) organophosphonic acids such as mono(2-ethylhexyl)ester of 2-ethylhexylphosphonic acid (PC 88A marketed by Daichi Chemicals); (c) organophosphinic acids such as di(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272 marketed by CYTEC corporation); (d) thiophosphoric acids such as di(2-ethylhexyl)dithiophosphoric acid (DTPA) (e) thiophosphonic acids such as di(2,2,4-trimethylphenyl)dithiophosphinic acid (CYANEX 301).

3) Ionizable crown ethers, such as crown ether carboxylic acid and crown ether phosphonic acid monoalkyl ester and naturally derived antibiotic macrocylces such as monesin, (Cusseler and Evans 1974).

In general the coordination complex of the chelating extractants with positively charged metal ions is very specific. Therefore, the chelating extractants can be used to achieve selective separation of metals. Although alkylphosphrous compounds, which are often called liquid cation exchangers, are less selective, they are less expensive as well and their metal complexes are more soluble in organic solvents than metal chelates. Therefore, they are also widely used in hydrometallurgical extraction processes.

With substitution of an alkyl-oxo group by an alkyl group, the acidities of the phosphorus compounds show the order of phosphoric > phosphonic > phosphinic, and thus their extraction abilities of cations are in the same order. The stripping tendencies for cations however are in the opposite order: phosphoric < phosphonic < phosphinic. This means that the relative low extraction ability of phosphonic or phosphinic extractants can be partially compensated by their high stripping tendency. In their study of rare earth extraction, Zhang and Xiao (1989, 1990) found that phosphonic acid had a lower extraction but higher stripping ability than D2EHPA as a result the net liquid membrane extraction efficiency of both extractants was similar.

The acidity of the external aqueous phase sometimes can seriously affect the choice of a suitable extractants. For instance, the Zinc effluent arising from spin baths in the viscous production has acidity up to a pH of 0.5. Under such a feed conditions D2EHPA, CYANEX 272 and PC 88A are unable to extract zinc efficiently. However Draxler and Marr (1986) found that DTPA could extract zinc effectively even at a pH of about 0.5, and they could resolve the problem satisfactorily.

Ionizable crown ethers bear ionizable carboxylic or phosphonic groups on the macro cycles. These macrocyclic compounds with ionizable protons are capable of facilitating cation transport by cation exchange mechanism without the need for an anion to accompany the cation macrocyclic complex across the liquid membrane or for an auxiliary complexing agent in the internal phase. This type of extractants seems to have good potential for commercial applications however their major drawback is availability and cost.

The extraction and stripping reactions for solute transport across the membrane by an acidic extractants can be represented as follows:

Extraction:

$$\underset{\text{aqueous phase}}{M^{2+}} + \underset{\text{organic phase}}{2HR} \longrightarrow \underset{\text{organic phase}}{MR_2} + \underset{\text{aqueous phase}}{2H^+} \quad \text{...... (2.2)}$$

Stripping:

$$\underset{\text{aqueous phase}}{2H^+} + \underset{\text{organic phase}}{MR_2} \longrightarrow \underset{\text{organic phase}}{2HR} + \underset{\text{aqueous phase}}{M^{2+}} \quad \text{...... (2.3)}$$

where HR is the protonated form of an acidic extractants, M^{2+} is the metal ion and H^+ the hydrogen ion. From these equations it is clear that the proton source is the driving force for transfer that pumps the metal ion against its own concentration gradient between the external and internal phases (Cussler 1971, Cussler, Evans and Matesich 1971, Schiffer *et al.* 1974a, 1974b).

Acids are generally used in the internal phase for stripping the solute from the membrane phase. In selecting suitable stripping acids, the effects of the acids on the liquid membrane extraction efficiency should be considered. In their study of rare earth extraction by D2EHPA in an ELM system with a polyamine as a surfactant, Zhang and Xiao (1989, 1990) found that a maximum extraction efficiency of rare earth was in the order of HCl $>HNO_3 >H_2SO_4$ at the same acid concentration, (6 N) in the internal phase. They observed that in the case of H_2SO_4 stripping, after the transfer of rare earths through the membrane phase into the internal phase, the stable complex anions $RE(SO_4)^{2-}$ and $RE(SO_4)_3^{-3}$ were formed and back extracted by the amine surfactant from the internal phase to the external phase. This lowered the overall efficiency of liquid membrane extraction. However, using HCL for stripping such stable complexes were not formed and hence the striped rare earth ions were restricted in the internal phase instead of being extracted by amine surfactants. When HNO_3 was used as a stripping acid it partially damaged the polyamine surfactants, causing an unstable membrane and thus the poor extraction efficiency (Zhang and Xiao 1989, 1990).

Basic extractions and their associated stripping agents

Basic extractants, the high molecular weight primary amines such as Primene JMT, secondary amine such as Amberlite LA-2, tertiary amines such as trioctylamine amine (TOA), tri-n-octylamine amine (TNOA) and Alamine 336 and the quaternary alkyl ammonium salts such as Aliquat 336, are used for the extraction of anionic or neutral metal complexes. These extractants are also regarded as liquid anion exchangers like alkyl phosphoric acids. For ELM metal extractions, primary and secondary amines show poor emulsion stability is usually not preferred. Thus the commercial tertiary amine Alamine 336 is widely used as extractant for acidic solutions and the commercial quaternary ammonium salt Aliquat 336 is employed for solutions with high pH.

The transport of metal anions through liquid membrane containing tertiary amines follows two possible mechanisms depending on the stripping agents employed:

- *Co-transport*

If a basic solution is used as a stripping agent in the internal aqueous phase, the permeation of metal anions proceeds according to the co-transport mechanism, in which the transport of metal anions across the membrane is coupled to the transport of hydrogen ions in the same direction with the following extraction and stripping reactions:

Extraction:

$$\underset{\substack{\text{organic}\\\text{phase}}}{R_3N} + \underset{\substack{\text{aqueous}\\\text{phase}}}{H^+ + A^-} \longrightarrow \underset{\substack{\text{organic}\\\text{phase}}}{R_3NHA} \qquad \ldots\ldots (2.4)$$

Stripping:

$$\underset{\substack{\text{organic}\\\text{phase}}}{R_3NHA} + \underset{\substack{\text{aqueous}\\\text{phase}}}{Na^+ + OH^-} \longrightarrow \underset{\substack{\text{organic}\\\text{phase}}}{R_3N} + \underset{\substack{\text{aqueous}\\\text{phase}}}{Na^+ + A^-} + H_2O \qquad \ldots\ldots (2.5)$$

where R_3N is the tertiary amine and A- is the metal anion.

- *Counter transport*

If an acid serves as the stripping agent in the internal aqueous phase, the permeation of metal anions obeys the counter transport mechanism, in which metal anions are transported in the direction opposite to the coupled anions with the following extraction and stripping reactions.

Extraction:

$$\underset{\substack{\text{organic}\\\text{phase}}}{R_3NHX} + \underset{\substack{\text{aqueous}\\\text{phase}}}{H^+ + A^-} \longrightarrow \underset{\substack{\text{organic}\\\text{phase}}}{R_3NHA} + \underset{\substack{\text{aqueous}\\\text{phase}}}{H^+ + X^-} \qquad \ldots\ldots (2.6)$$

Stripping:

$$\underset{\substack{\text{organic}\\\text{phase}}}{R_3NHA} + \underset{\substack{\text{aqueous}\\\text{phase}}}{H^+ + X^-} \longrightarrow \underset{\substack{\text{organic}\\\text{phase}}}{R_3NHX} + \underset{\substack{\text{aqueous}\\\text{phase}}}{H^+ + A^-} \qquad \ldots\ldots (2.7)$$

where R_3NHX is the amine salt, A^- is the metal anion and X^- is the couple anion. According to the counter transport stripping equation, acid stripping regenerates the amine salts for re-extracting metal anions from the external aqueous phase.

Kitagawa *et al.* (1977) believed that both mechanisms can be used successfully in ELMs. But Hirato *et al.* (1990) have found that the co-transport type extraction can give a far better result than that of counter transport for the extraction of U(VI) and Mo(VI) by the tertiary amine, tri-n-octylamine amine in the ELM systems. Usually the concentration of amine extractants in the membrane phase should not be very high. High concentrates of amine extractants in the membrane phase have been observed to lead to high osmotic swelling and high rate of membrane breakdown. A major drawback for extraction of metal anions is the poor selectivity of amine extractants to different anions as observed by Draxler and Marr (1986).

Neutral extractants and their associate stripping agents

Neutral extractants often extract uncharged metal complexes or cations together with the coupled anions in order to maintain the electrical neutrality. In this type of extraction, the metals species is coordinated with 2 different types of ligands - a water soluble anion and an organic soluble electron donating functional group. Most of the neutral extractants that have been investigated in the liquid membrane studies are organo-phosphoryl compounds such as tri-n-butyl phosphate (TBP), tri-n-butyl phosphine oxide (TBPO) and tri-n-octylphosphine oxide (TOPO). These compounds are used extensively as extractants for the separation of actinides and lanthanides. They are specially used for recovery of uranium and plutonium in the spent fuel reprocessing of nuclear plants.

In liquid membrane systems containing acidic or basic extractants as carriers, hydrogen ions or hydroxide ions are used to generate the driving force for solute permeation across the membrane. For liquid membrane with neutral carriers, however other driving forces have to be used instead of pH gradient. Usually strong metal complexing agents in the internal aqueous phase are used to accomplish this. The stability complex of the metal complex for stripping must be higher than that of the metal complex for extraction so as to provide the high driving force for metal transport.

The transport mechanism for solute across the liquid membrane incorporated with a neutral extractant is expressed by the following extraction and stripping reactions:

Extraction:
$$\underset{\text{aqueous phase}}{M^{+} + A^{-}} + \underset{\text{organic phase}}{L} \longrightarrow \underset{\text{organic phase}}{MLA} \qquad \text{...... (2.8)}$$

where M^{+} is the metal ion, A^{-} is the co-anion, and L the neutral extractant.

Stripping:
$$\underset{\text{organic phase}}{MLA} + \underset{\text{aqueous phase}}{M_S^{+} + R^{-}} \longrightarrow \underset{\text{organic phase}}{L} + \underset{\text{aqueous phase}}{MR + M_S^{+} + A^{-}} \qquad \text{...... (2.9)}$$

where R^{-} is the anion complexing agent and M_S^{+} the co-cation.

The neutral extractants serves as a carrier to shuttle cations across the membrane phase, while the anion complexing agent in the internal aqueous phase provides a sink for cations by complexation. This complexation lowers the concentration of the free (unbounded) cations in the internal phase and maintains the concentration gradient driving phase across the membrane phase, which is necessary for the transport. Under favorable conditions the free cation concentration in the internal phase within transport will be essentially zero and a concentration gradient will be maintained until the external phase is depleted of the cations (Izatt *et al.* 1984).

2.3.4 Emulsion liquid membrane formation and post extraction processes.

Emulsion liquid membranes are prepared by dispersing the inner receiving phase in an immiscible liquid membrane phase to form an emulsion. Marr and Kopp (1982) have provided a set of quantitative guidelines for the formation of stable water-in-oil ELMs based on the surfactant HLB, surfactant concentration, organic viscosity, and volume ratios of the various phases as listed below:

- Organic phase soluble surfactant concentration 0.1 to 5 wt % and HLB value 6 to 8
- Organic phase viscosity 30 to 1000 mPa.s.
- Volume ratio of the internal receiving phase to membrane phase 0.2 to 2.0
- Volume ratio of internal phase to continuous external phase 0.05 to 0.2 and volume ratio continuous phase to emulsion phase 1 to 40.

When the emulsion is dispersed by mild agitation in a continuous phase, many small globules of emulsions are formed. These globules are stable and do not disintegrate when system is agitated. The size of the globules depends strongly on the nature and concentration of surfactant in the emulsion, the emulsion viscosity and the mode of intensity of mixing. Usually, the size of globules ranges in order of one to two mm in diameter. Each emulsion globule contains many tiny encapsulated droplets with a typical size of one micron in diameter. A large number of globules of emulsion can easily be formed to produce a correspondingly large membrane surface area for rapid mass transfer from either continuous phase to the encapsulated phase or vice versa.

There are many suitable devices available such as high pressure homogenizers or devices using the rotor / stator principle such as colloid mill to prepare emulsions. Main disadvantages of conventional high pressure homogenizers and colloid mills are the resulting broad droplet size distribution and high mechanical stress due to the forces in the flow field. The second point may cause problems when emulsions containing stress sensitive ingredients needs to be produced. Further in the liquid emulsion membrane process often very acidic stripping phases require to be emulsified this causes corrosion problems which makes the process expensive. In order to increase the efficiency of the emulsification process, different methods for emulsification have been developed and adapted over the years. Nakashima *et al.* (1991) introduced membrane emulsification techniques in the early 1990s where one phase is dispersed into the other phase by being pressed through the pores of a membrane. The detachment of the droplets on the membrane surface results in the production of an emulsion with a narrow droplet size distribution at mild process conditions.

The fast progress in micro engineering and semi conductor technology enabled the development of custom-designed micro channels, that Nakajima and co-workers (1997) applied in emulsification technology. The special geometry of those micro channels causes the formation of uniform size droplets by the Laplace instability. Since no additional forces for the droplet detachment are necessary, process conditions in micro channel emulsification are even milder than in membrane emulsification.

Subsequent to emulsification the emulsion and feed phase are contacted for a defined time interval under conditions of mild agitation. As mentioned earlier this leads to the emulsion being dispersed finely in the continuous feed phase. After the contact time is over the agitation of the feed phase is stopped this leads to separation of the emulsion and the feed phase. The separation of the emulsion from the feed is achieved by decantation. The emulsion containing the loaded solute needs to be further treated to recover the solute as well as to recycle some of the emulsion components. It is essential to break the emulsion into its oil and aqueous components. The oil phase containing the emulsifier and the carrier has to be recycled after necessary make up to achieve while the aqueous phase may be subjected to processes like electrowinning or precipitation to recover the metal values.

2.3.5 Splitting of Emulsions (Demulsification)

Demulsification is one of the critical processes of emulsion liquid membrane technique. Demulsification is necessary to recover the encapsulated solute as well as for the recycle of membrane components without which there is no chance of attaining economic advantage from the process. Emulsions are thermodynamically unstable systems. The instability of emulsion is greatly affected by the nature of the surfactant film that is strongly dependent on surfactant adsorption, interfacial tension and viscosity. Generally, the demulsification of water-in-oil emulsion consists of two processes. One is coagulation and second is coalescence. In the first case disperse droplets in the emulsion come together and reduce the total interfacial area but do not combine to form a single drop of greater volume, while in the second case bigger droplets form and the emulsions are disrupted as a result. In general demulsification of water-in-oil emulsions is mainly influenced by three physical characteristics of internal droplet size, surfactant concentration and oil viscosity. Demulsification rate is affected by both the emulsion preparation and demulsification condition. To demulsify completely and quickly, some additional forces are required.

Two principal approaches for the demulsification of the loaded emulsion are chemical and physical treatments. Chemical treatment involves the addition of a demulsifier to the emulsion. However, the added demulsifier will change the property of the surfactant and change its emulsification power and thus prohibit its reuse. Therefore, chemical treatment is not suitable for breaking liquid membrane emulsions. Physical treatment methods include heating, centrifugation, ultrasonic, solvent dissolution, high shear, and the use of high-voltage electrostatic fields. The two major demulsification techniques are reviewed below:

2.3.5.1 Heat Treatment

Heat treatment of the emulsion is an effective method of demulsification because it reduces the viscosity and density of oil. The oil density decreases faster than the density of water because the oil has a large coefficient of expansion than water. Elevated temperature also increases the solubility of surfactants in both water and oil phases, thus weakening the interfacial film. The major drawback of heat treatment is slow demulsification kinetics (Lissant 1983).

Microwave heating technology is an interesting variant that has been successfully tested in field operation and laboratory tests for the demulsification of oil–water–solid emulsion Fang *et al.* (1998). They believed that microwave-induced molecular rotations reduce the zeta potential, which suspends water droplets and solid particles in an emulsion, and that was considered to play a role in addition to the primary heating effect in the acceleration of microwave demulsification. One important characteristic of microwave heating is that the entire volume of sample is heated up internally. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy does not rely on diffusion of heat from the surfaces, and it is possible to achieve rapid and uniform heating of thick materials. In addition to volumetric heating, microwaves can be utilized for selective heating of materials.

2.3.5.2 Electrostatic Coalescence Treatment

Electrostatic coalescence is a technique which is widely used to separate dispersed aqueous droplets from non-conducting oils. The petroleum industry has been using it to separate brine emulsified in crude oil; the chemical industry used it to resolve water-in-oil emulsion generated during extraction. Since this type of demulsification is strictly a physical coalescence process, the technique is most suitable for breaking W/O emulsion used in liquid membrane technology (Frankenfeld *et al.* 1981, Hayworth *et al.* 1983, Hsu *et al.* 1983).

An electric field has several effects on water droplets dispersed in oil phase. The insulative nature of the continuous oil phase allows the establishment of a high electric field cross the emulsion. This electric field can polarize and elongate the water droplets. It can be cause unidirectional migration of the droplets in the dilute emulsions by either an electrophoresis mechanism or a dielectrophoresis mechanism. When the concentration of droplets becomes high, it can also cause the coalescence of the droplets into larger droplets. At very high electric field strengths, a single water droplet could also burst into several small droplets.

The use of electrostatic coalescence to separate LM emulsions is different from the conventional application of such coalescence. First the LM emulsions contain much more aqueous phase and the recovered oil may contain more water than pipeline quality dehydrated crude. Second, since these emulsions are intentionally made, they contain high concentration of potent emulsifying surfactants. Finally, the properties of the oil phase must be preserved for re-emulsification.

The entire emulsion breaking process can be divided into three stages. The first stage involves droplet coalescence and growth, the second stage involves droplet settling, and third stage involves coalescence of the large water and oil droplets with their respective continuous phases in the coalescer. Coalescer throughput can be limited by any of these three stages because of the intentional incorporation of potent surfactants in ELM systems to stabilize the emulsions; the ELM emulsions have a very high tendency to form residual sponge emulsions during electrostatic coalescence. This makes it impractical to break the LM emulsions with a conventional electrostatic coalescer equipped with bare metal electrodes necessitating the use of insulated electrodes. Two major parameters are used to quantify the coalescence: the emulsion feed rate and the water remaining in the recovered oil. The higher the feed rate, the more the water would remain in the recovered oil. For stable LM emulsions, however, there exists a maximum emulsion feeding rate above which a layer of sponge emulsion begins to form at the oil / water interface of the coalescer, indicating the onset of a coalescence upset. Thus the maximum steady state coalescence rate of a coalescer is limited by the onset of sponge emulsion formation.

In addition to compositional variables which determine the coalescibility of a specific emulsion, the performance of the coalescer also depends upon many operating variables, e.g. the applied voltage, the aqueous concentration, the emulsion feed, the position of the feed inlet and the separation between the glass electrode and the oil / water interface.

There exists a variety of other demulsification techniques some are in the physical domain viz. using hydrophilic porous glass membrane (Sun *et al.* 1998) and other techniques in the chemical / biochemical domain since reuse of membrane phase is an economic necessity for the success of ELM technique therefore Chemical/biochemical techniques are not considered for destabilization of emulsions. On the whole it appears that demulsification with electrostatic fields appears to be the most efficient and economic way for breaking W/O emulsion in the liquid membrane process (Gu *et al.* 1992).

2.4 Metal extraction using emulsion liquid membranes

Metal extractions using ELMs have been in existence since 1970's a large number of metals have been extracted using this technique. One monogram on the overall disposition of metal extraction using ELMs have also been published (Bartsch and Way 1996) and a number of review papers have summarized the trends from time to time (Gu *et al.* 1992). In general it is observed that extraction of copper from acidic media has been very widely investigated followed by rare earths and other transition metals such as chromium etc. An attempt to summarize the entire work done in this field is beyond the scope of this study, hence it is attempted to list out the recent work on the extraction of various metals using ELM technique along with the membrane components and stripping agent in Table 2.5.

2.5 Commercial applications of ELM technology

Emulsion liquid membrane technology has somehow not made the type of commercial impact that was anticipated from the technique when it was nascent. Current commercial applications include the removal of zinc, phenol, and cyanide from wastewaters.

1 Draxler and Marr (1986) discuss the application of ELM technology for zinc removal as a zinc sulphate from low concentration wastewater streams of viscose fiber industry in Lenzing AG in Austria, Glanztoff in Austria, CFK Schwarza in Germany and AKZO / Ede in The Netherlands.

2 Zhang and Coworkers (Zhang, Liu and Lu 1987, Zhang et al. 1988a, 1988b) described a commercial application for ELMs in China for phenol removal from wastewater streams at Nanschung plastic factory Guangzhous in China.

3 Marr, Bart and Draxler (1990) describe the removal of heavy metals including Zn, Cd, Cu, Pb and Hg from wastewater and the recovery of Ni from spent electroplating solutions and rinse water (Draxler and Marr 1986, Marr, Lackner and Bart 1989).

4 Cyanide removal from wastewater in gold processing plant at China and well control fluid from Exxon to prevent well blow down.

In addition to these pilot plant scale work on the recovery of copper from run of mine waste waters and low grade leach solutions using emulsion liquid membrane system was field tested at a copper mine by US Bureau of Mines as described by Wright *et al.* (1995). Many applications in wastewater treatment, separation of organic acid and antibiotic recovery from fermentation broths, rare earth metal extraction and radioactive material removal, have considerable potential for large scale applications.

Table 2.5 Compositions and conditions of emulsion liquid membrane for heavy metal removal from aqueous streams

Solute	**Surfactant**	**Extractant**	**Internal phase**	**Diluent**	**Reference**
Cu	PA 18	Acorga	H_2SO_4	Shellsol T	Draxler and Marr 1986, Draxler *et al.* 1988
Cu	Span 80	LIX 64N or SME 529	H_2SO_4	Shellsol T	Martin and Davies 1977
Cu	ENJ 3029, Paranox 100	LIX 64N Acorga P5100	H_2SO_4	S100N, LOPS Isopar M	Li *et al.* 1983
Cu	ECA4360J, Span 80 etc.	LIX 65N	H_2SO_4	n-haptane	Nakashio *et al.* 1988
Cu	Span 80	LIX 984N-C	H_2SO_4	Kerosene	Sengupta *et al.* 2006
Cu	Span 80	LIX 84	H_2SO_4	Kerosene	Sengupta *et al.* 2006
Cu	Span 80	LIX 84I	H_2SO_4	Kerosene	Sengupta *et al.* 2007
Cu	Span 80	LIX 622,LIX 84	H_2SO_4	Kerosene	Chakravarti *et al.* 2000
Cu	Span 80	D_2EHPA	$CuSO_4$ and disodium salt of EDTA	Kerosene	Juang *et al.* 2004
Cu	Span 80	LIX860N-IC	H_2SO_4	Kerosene	Valenzuela *et al.* 2005, 2009,
Cu	ECA4360J	LIX 54, LIX84I	H_2SO_4	Shellsol T	Gameiro *et al.* 2007
Cu	Span 80	D2EHPA	H_2SO_4	Hexane, dodacane, heptanes	Chiha et. al. 2010
Cu	Span 80	LIX 860	H_2SO_4	Kerosene	Laxarova *et al.* 1993
Cu	ECA 11522	Acorga PT5050	H_2SO_4	Shellsol T	Bart *et al.* 1988
Cu	Span 85, Brij 72 Span 80, Arlacel83	LIX65N, LIX63	H_2SO_4	Cyclohexane	Mikucki *et al.* 1986

Continued….

Cu	Span 20, Span 80, Crill 4	LIX 64N, Shell SME 529	H_2SO_4	Napoleum 470, Chlorinated solvents, Esso Escaid	Martin *et al.* 1977
Cu	Paranox 100	P5100	H_2SO_4	50-50 % Isopar M & V	Wright *et al.* 1995
Cu	Span 80	LIX 64N	H_2SO_4	Kerosene	Volkel *et al.* 1980
Cu	Span 80	D2EHPA	KNO_3	Polybutadiene in Cyclohexane	Strzelbicki *et al.* 1997
Cu	Span 80	D2EHPA	HCl	Kerosene (80 % v/v) with n-heptane (5 % v/v)	Chakraborty *et al.* 2003
Cu	Polyamine ECA 4360J	LIX 84-I and LIX 54	H_2SO_4	Shellsol T	Gameiro *et al.* 2010
Cu	Sodium dodecyl sulfate, SDBS, HDTMAB	N,N-is(salicylidene)naphthylene 1,8-diamine	EDTA, KSCN, KI, $Na_2S_2O_3$, $Na_2C_2O_4$, HNO_3, HCl, $HClO_4$, H_2SO_4 etc.	Chloroform	Rouhollahi *et al.* 2007
Zn	ECA4360J	D_2EHTPA	H_2SO_4, LiCl	Paraffinic solvent	Reis *et al.* 2004
Zn	Span 80	D_2EHPA	H_2SO_4	Kerosene	Valenzuela *et al.* 2007
Zn	Span 80	PC 88A	HCl	Kerosene	Valenzuela *et al.* 2005
Zn	Span 80	PC 88A	H_2SO_4	n-heptane	Goto *et al.* 1991
Zn	Span 80	Bis(2ethylhexy) phosphoric acid	H_2SO_4	n-haptane	Uribe *et al.* 1988
Zn	Span 80, ECA 4360N	D_2EHPA, DEHMTPA	H_2SO_4 or NaOH	n-dodecane	Bart *et al.* 1995
Zn	ECA 4360	DTPA	H_2SO_4	Shellsol T	Draxler and Marr 1986

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Zn	PX 100	DTPA	H_2SO_4	Shellsol T	Draxler, Furst and Marr, 1988
Ni	Span 80	DBHQ	H_2SO_4	Kerosene	Kumbasar *et al.* 2009
Ni	Span 80	D_2EHPA	H_2SO_4, NaOH, HCl	Kerosene, n-heptane	Chakraborty *et al.*2004
Ni	ECA4360J	HQ	EDTA	Kerosene	Kumbasar *et al.* 2009
Ni	Span 80	D_2EHPA	H_2SO_4	n-haptane	Juang *et al.* 1995
Ni	Monemul 80	D_2EHPA	HNO_3	Mixture of xylene isomers, heptane, toluene, dodecane	Kulkarni *et al.* 2000
Ni	ECA 4360, Span 80	DTPA	H_2SO_4	Shellsol T	Draxler and Marr 1986
Cd	Span 80	TOA	NaOH	O-xylene	Li *et al.* 1997
Cd	Span 80	D_2EHPA	HNO_3	Bayol 92	Sznejer *et al.* 1999
Cd	Span 80	TOA	NH_4OH	Kerosene	Kumbasar *et al.* 2009
Cd	Span 80	D_2EHPA	HCl	Kerosene	Basualto *et al.* 2006
Cd	Span 80	Aliquat 336	NH_4OH	Kerosene	Kumbasar *et al.* 2008
Cd	ECA 4360J	Alamine 304	HCl, NaCl	kerosene	Witkamp *et al.* 2000
Cd	Arlacel C	CYANEX 302,	NaCl, HCl mixture	Kerosene	Lizon *et al.* 2000
Cd	Span 80, Polyamine	Aliquat 336	EDTA	S100N	Weiss *et al.* 1982, Kitagawa *et al.* 1977
Co	ECA4360J	TOA	H_2SO_4	Kerosene	Kumbasar *et al.* 2010
Co	ECA4360J	TIOA	H_2SO_4	Kerosene	Kumbasar *et al.* 2009
Co	Span 80	CYANEX923	H_2SO_4	Cyclohexane	Gasser *et al.* 2008
Co	ECA4360J	PC 88A	HCl	Kerosene	Kumbasar *et al.* 2009
Co	Span 80	DBHQ	H_2SO_4	Kerosene	Kumbasar *et al.* 2008
Co	Span 80	TOPO	NH_4OH	Kerosene	Kumbasar *et al.* 2009

Continued….

Co	Span 80	TBP	NH_4OH	Kerosene	Kumbasar *et al.* 2009
Co	PX100	PC 88A	H_2SO_4	n-heptane	Kasaini *et al.* 1998
Co	ECA 4360	CYANEX 302	H_2SO_4	Escaid 110	Salum *et al.* 2004
Co	Span 80	D_2EHPA	H_2SO_4	Kerosene / Shellsol T	Nemeh *et al.* 1993
Co	Span 80	D_2EHPA	HNO_3	Cyclohexane	Strzelbicki 1978
Co	ECA 4360	D_2EHPA	H_2SO_4	LOPS	Gu *et al.* 1986
Co	Span 80	LIX 64N	EDTA	Toluene	Macasek *et al.* 1984
Cr	ECA4360J	TOA	$(NH_4)_2CO_3$	Kerosene	Kumbasar *et al.* 2008
Cr	ECA4360J	Alamine336	$(NH_4)_2CO_3$	Kerosene	Kumbasar *et al.* 2008
Cr	Span84,ArlacelA	TOPO	NaOH	Cyclohexane	Hasan *et al.* 2009
Cr	Span 80	TBP	NaOH	Hexane, heptanes, dodecane	Chiha *et. al.* 2006
Cr	Span 80	DEPA	H_2SO_4	Kerosene	Saravanan *et al.* 2006
Cr	Span 80	Alamine336	NaOH	Kerosene	Chakraborty *et al.*2005
Cr	Paranox 106	Aliquat 336	NaOH	Kerosene	Banerjea *et al.* 2001
Cr	Span 80	TOA	KOH	Kerosene	Rajasimman *et al.*2010
Cr	Span 80	Aliquat 336	H_2SO_4, NaOH etc.	Kerosene / liquid paraffin	Chakravarti *et al.* 1995
Cr	Span 80	Aliquat 336	NaOH	Kerosene	Datta *et al.* 2001
Cr	Span 80	Aliquat 336	KOH	Kerosene	Rajasimman *et al.*2009
Cr	Paranox 106	Aliquat 336	NaOH	Kerosene	Irabien *et al.* 1992
Cr	Span 80	Aliquat 336	NaOH	Isoparaffin	Kitagawa *et al.* 1977
Cr	LMS-2	TOA	NaOH	Kerosene	Zhang *et al.* 1988a
Cr	Span 80	TBP	NaOH	n-hexane	Vohra *et al.* 1989
Ag	Span 80	D_2EHPA	H_3PO_2	Kerosene	Tang *et al.* 2009
Ag	Span 80	CYANEX 302	H_2SO_4	Kerosene	Othman *et al.* 2006
Ag	Span 80	D_2EHPA	H_2SO_4, HCl, HNO_3	Kerosene	Lee *et al.* 1996

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Ag	Span 80	DC18C6	$Li_2S_2O_3$	Toluene	Christensen *et al.* 1983
Au	LK 80	MIBK	NaOH, Na_2SO_3	Liquid paraffin	Kargari *et al.* 2004
Au	Polyamine E644	N503	Na_2SO_3, NaOH	kerosene	Nianxi Yan 1993
Pd	Span 80	DDTPA	Thiourea	n-heptane	Kakoi *et al.* 1993
Pd	Span 80,PX 100	MSP-8	Thiourea	n-heptane	Kakoi *et al.* 1996
U	Span 80	TOPO	Na_2CO_3	Paraffin	Kulkarni *et al.* 2002
U	Span 80	Aliquat 336	Na_2CO_3	Kerosene	El Sayed *et al.* 2003
U	ECA4360J	N-alkyl-caprolactam	Na_2CO_3	n-dodecane	Yang *et al.* 2005
Ga	ECA4360J	TBP	HCl	Kerosene	Kumbasar *et al.* 2004
Hg	Span 80	TOA	NaOH	Toluene	Li *et al.* 1996
Hg	Rofetan OM	1,1-Dibutyl-3-benzoylthiourea	HCl	Decane	Weiss *et al.* 1982
Pb	Span 80	D2EHPA	H_2SO_4	Kerosene	Sabry *et al.* 2007
Pb	Span 80	DC18C6	$Li_2S_2O_3$	Toluene	Christensen et al. 1983
Fe	Span 80	$CH_3(C_8H_{17})_3NCl$	HCl	Toluene	Ohki *et al.* 1983
Ar	ECA 4360J	2-ethylhexyl alcohol	NaOH	Heptane, Exxsol D-80, Isopar M	Huang *et al.* 2009, 1996
Indium	Span 80	Di-isostearyl-phosphoric acid	HCl	n-haptane	Kondo *et al.* 1998
Gd	Span 80	8-hydroxy-quinoline	HNO_3	Toluene	Hasan *et al.* 2009
Cs	Span 80 / 85	Crown ether	Ephedrine	Xylene	El-Said *et al.* 2003
Cs	Span 80 / 85	8,8-dibromo-bis(1, 2 dicarbolly)	Sodium citrate	Notrobenzene	Macasek *et al.* 1984

Continued….

Ce	Span 80 / 20	TOPO	Cyclohexane	Sodium citrate	Macasek *et al.* 1984
Mo	Polyamine, Monesan	Aliquat 336	NaOH	Xylene, heptane, dodacane, and kerosene mixture	Kulkarni *et al.* 2002
Ru	Monemul, Span 80	TOA	Perchloric acid	Liquid paraffin	Kankekar *et al.* 2010
Ge	ECA 4360J, Span 80	Kelex 100	NaOH	Toluene, STA90 NS, Escaid 110	Tutkun *et al.* 1999
Eu	Span 80	D_2EHPA	HNO_3	Kerosene / Polybutadiene	Yu *et al.* 1986
Eu	Span 80	PC-88A	HCl	n-dodecane	Lee *et al.* 1994
Sr	Span 80 / 85	Br_2DCC	Sodium citrate	Nitrobenzene	Macasek *et al.* 1984
Tc	Span 80	Aliquat 336	Cyclohexane	$NaClO_4$	Macasek *et al.* 1984
Vanadium	Succimide derivative	TNOA	Na_2CO_3	Kerosene	Zheng *et al.* 1988
Rare earth metals	Span 80	PC 88A	H_2SO_4	n-haptane	Uezu *et al.* 1997
Rare earth ions	LMS 2	Di-2-ethylhexyl phosphoric acid	HCl	Kerosene	Liu *et al.* 1997
Rare earth metals	Span 80 and PX 100	PC-88A	H_2SO_4	n-heptane	Goto *et al.* 1993
Rare earth metals	Span 80	Carboxylic crown ether	HNO_3	Mixture of mineral oil and toluene	Tang *et al.* 1989
Cu, Zn	Span 80	D_2EHPA	H_2SO_4	Isododacane	Fouad *et al.* 2008
Cu, Zn	Span 80, ECA4360J	LIX 64N	H_2SO_4	Kerosene	Kataoka *et al.* 1989
Cu, Zn	Span 80	bis(2-ethylhexyl phosphate)	H_2SO_4	Kerosene	Meera Sheriffa Begum *et al.* 2007

Continued….

Cu, Cd	Arlacel C	CYANEX 302	HCl	kerosene	Urtiaga *et al.* 2000
Cu, Zn, Ni	ECA 5025, DNP-8	LIX 860, LIX 984, CYANEX 272, D_2EHPA	H_2SO_4	Tetradecane	Raghuraman *et al.* 1994
Cu, Mg, Fe, Al	Polyamine	LIX 64N	H_2SO_4	S100	Frankenfeld *et al*. 1981, Cahn *et al*. 1981
Cu, Zn, Cd, Fe, Co, Ni, Mn	Span 80	LIX 64N, D_2EHPA, Acorga P 5300, Acorga P 5100	H_2SO_4	Kerosene	Schugerl *et al.* 1985
Cu, Ni, Co	PEG	PEG	KOH	1,2 dichloroethane	Uddin *et al.* 2000
Cu, Pb, Mn, Co, Ni, Cr	Span 80	8-Quinolinol	HCl	Toluene	Kageyama *et al.* 2004
Cu, Ni, Co, Cd	Span 80	8-Quinolinol	HCl	Toluene	Matsumiya *et al.* 2004
Cu, Fe, Mn, Cd, Ni, Cu, Pb, Zn	Span 80	D_2EHPA, PC 88A	H_2SO_4, HCl	Kerosene	Li *et al.* 1993
Cu, Fe, Zn, Co	Paranox 100, Paranox 106, PA-18	P5100, LIX 64N	H_2SO_4	Isopolar L	Nilsen *et al.* 1991
					Table continued
Co, Ni	Span 80	TOPO	NH_3	Kerosene	Kumbasar *et al.* 2009
Co, Ni	ECA4360J	Alamine300	NH_4OH	Kerosene	Kumbasar *et al.* 2008

Continued….

Co, Ni	Span 80, PX 100	D2EHPA, PC 88A	H_2SO_4	n-heptane	Kasaini *et al.* 1998
Co, Ni	L113A	P204	HCl	Mixture of kerosene and paraffin	Longquan *et al.* 1997
Cd, Pb	ECA5025	D_2EHPA	H_2SO_4, HCl	Tetradecane	Raghuraman *et al.*1995
Cd, Ni	Span 80	D_2EHPA	H_2SO_4	Kerosene	Yanlin *et al.* 2010
Pt, Pd	Span 80, PX 100	TLA, TBP TOMAC, TOPO, TIBPS	HCl	n-heptane	Kakoi *et al.* 1996
U, Fe, Ca, Mg, Mn	Span 80	Alamine 336	Na_2CO_3	Light and heavy paraffins	Kulkarni *et al.* 2009
U, Fe, Ca, Mg	Span 80	TOPO, TBP, D_2EHPA	HNO_3	Paraffin	Kulkarni, 2003
La, Nd	Span 80, PX 100	PC 88A	H_2SO_4	n-heptane	Goto *et al.* 1989
Ba, Mg, Ca, Sr	Span 80	Carboxylic crown ether	HCl	Mineral oil / Toluene	Bartsch *et al.* 1984
Au, Pt, Pd, Ag, Cu, Pb, Fe	Polyamine	N 503	Na_2SO_3	Kerosene / Paraffin	Yan *et al.* 1990

2.6 Conclusions

It’s been forty five years since the first application of ELM technology was described for metal extraction from waste water streams by Frankenfeld and Li (1987). Despite its numerous advantages the ELM technology did not achieve widespread application in metal extraction as expected by its exponents and early workers. Perhaps the main reason was the difficulties related to handling the emulsion and reclamation of the metal from the emulsion.

Over the years extensive work on metal extraction using ELM techniques has lead to establishment of a volume of knowledge that has reduced the extent of uncertainty of the intricacies of this technology. It also helped to realize that ELM technology would not function as an alternate to solvent extraction of metals, rather ELM technology has to create a niche for itself within the domain of solvent extraction of metals such that difficult or unique separations where solvent extraction is not the best option could be handled by ELM techniques. This would as well justify the additional effort needed to handle the emulsion.

Some niche areas where ELM technology can be effectively used are the following:

i. Extraction and purification of rare earths and radio nucleotides which are low on volume but high on cost materials.

ii. Recovery of metals from printed circuit board spent etchants where ammonia is widely used as the leachant. These are again small volume jobs necessary to meet the environmental requirements and do not justify large inventory of solvents and extractants.

iii. Separation of binary metal solutions such as the removal of cadmium from zinc run of mine waters keeping in view that zinc and cadmium almost always appear together in deposits.

Additionally, literature survey reveals that information on the simultaneous extraction and selective removal of metals from binary mixtures using ELMs is indeed scarce, there is considerable scope to use the ELM technology for separation as well as enrichment of specific metal cations from mixture of metals. Further it is observed that ELM system often introduces an element of selectivity by virtue of its construct to systems where due to absence of specific metal extractants the separation by solvent extraction is not selective.

The major success story for ELM separation is the removal of zinc from viscose fiber industry. In order to consolidate this effort and replicate it economically at other locations the technique needs to be improvised particularly by changing the extractant from DIPA to some other easily strippable extractant. Problems related to emulsion swelling and stability are persistent in most systems.

In order to address these challenges and problems this investigation was undertaken.

CHAPTER 3
MATERIALS AND METHODS

The experimental and analytical methods used in this investigation for the extraction of heavy metal ions from aqueous solutions into emulsion liquid membranes is described in this Chapter. It also records the parameters used for characterization of the W/O emulsions that were used as the emulsion membrane and finally it specifies the techniques adopted to study the bonding in the extractant- metal complexes.

3.1 Materials and reagents

3.1.1 Membrane materials

- *Oil phase*

The liquid-membrane phase – the oil phase of the W/O emulsion, was formulated by incorporating a surfactant and a metal extractant in an organic diluent. Commercial kerosene was used as the membrane material, it had a boiling range 152°C – 271°C and contained n-paraffins (27.1%), naphthenes (55.9%), aromatics (16%) and olefins (1%) having density (ρ_{15}) of 821.3 kg / m^3. Kerosene was used as supplied by Indian Oil Corporation Limited.

- *Emulsifier*

Span 80 generically known as Sorbitan monooleate ($C_{24}H_{44}O_6$) having MW 428.61 was the non-ionic surfactant used for stabilizing the emulsion. It had density 986 kg / m^3, refractive index 1.48, flash point >110 ºC, saponification value from 145 to 160, water content less than 1% and was supplied by S. D. Fine Chemicals Limited. The chemical structure of Span 80 is shown in Fig. 3.1

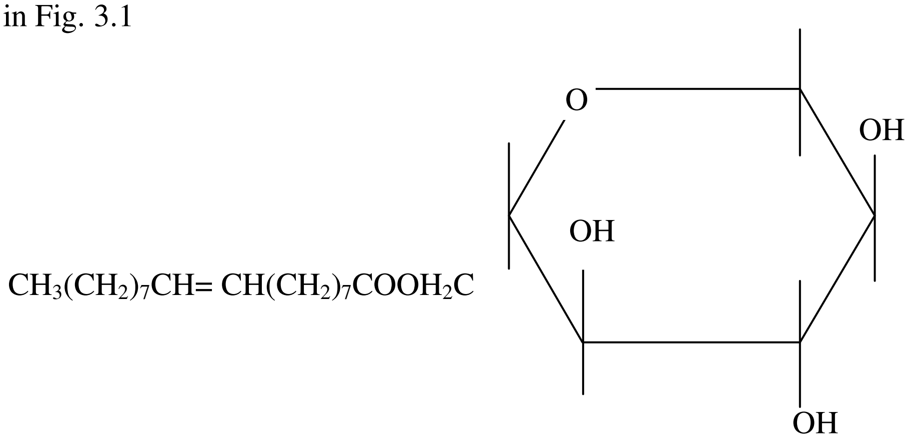


Fig. 3.1 Sorbitan monooleate (Span 80)

- Carrier

Carriers are metal extractants; they are in general classified on the basis of structure, acidity, extraction and stripping chemistry. The five main types of extractants commercially available for metal extraction are (1) Chelating agents, (2) Ion pair extractants, (3) Neutral or solvating extractants, (4) Organic acid extractants and (5) Ligand substitution extractants. Chelating oxime extractants and the organic acid extractants operate on a hydrogen ion cycle, extracting metals over a specific pH range and stripping at lower pH. The extraction and stripping pH isotherms for individual metals differ and this provides an opportunity for selective extraction. In the present study four different extractants were used for metal extraction as listed below.

D2EHPA

Di (2-ethylhexyl) phosphoric acid 95% minimum with Mono (2-ethylhexyl) phosphoric acid less than 2% was obtained from Fluka, Germany as well as Merck Specialties Private Limited, Germany. D_2EHPA is an acidic extractant and extracts a wide range of metals. Its molecules predominate as monomers in aromatic diluents and as dimers when dissolved in aliphatic diluents. Usually aliphatic diluents are preferred for extraction processes due to their lower toxicity. Selectivity of D2EHPA for metal ions is poor, hence, careful pH control is required to achieve reasonable selectivity.

Physical data: Molecular formula: $C_{16}H_{35}O_4P$, Molecular weight: 322.4, Appearance: clear to colorless to yellow liquid, Texture: oily, Odor: odorless, Flash point: 206 °C, Lighting point: 233 °C, Solidifying point: - 50 °C, Density at 25 °C: ~ 0.97 g/cm^3, Viscosity: 40 mPa s.

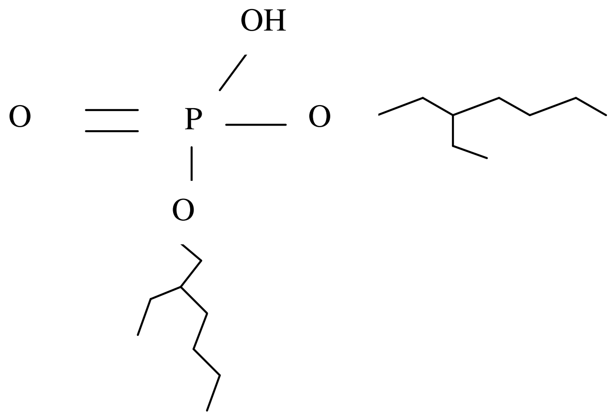


Fig. 3.2 Di (2-ethylhexyl) phosphoric acid (D_2EHPA)

CYANEX 302®

Cyanex 302 (Di (2, 4, 4,) trimethylpentyl monothiophosphinic acid) is a phosphinic derivative of phosphoric acid, where one sulfur atom replaces one of the oxygen atoms bonded to the phosphorus as shown in Fig.3.3. The extractant was supplied by Cytec Limited, Canada, it has an active component content of 84 %. Cyanex 302 is usually used in the industry for the separation of Co from Ni in feed mixtures containing cobalt and nickel. It is specific towards Co, it is known for the difficulty to strip the metal values from it which is its drawback.

Physical data: Molecular formula: $C_{16}H_{34}PSOH$ Molecular weight: 306, Appearance: Pale yellow liquid, Texture: oily, Odor: faintly characteristic of hydrogen sulfide, Flash point: > 96 °C, Lighting point: 393 °C, Solidifying point: - 20 °C, Specific gravity at 25 °C: 0.93, Viscosity at 25 °C: 195 cP, Water solubility: 3 mg / liter at 50^0 C.

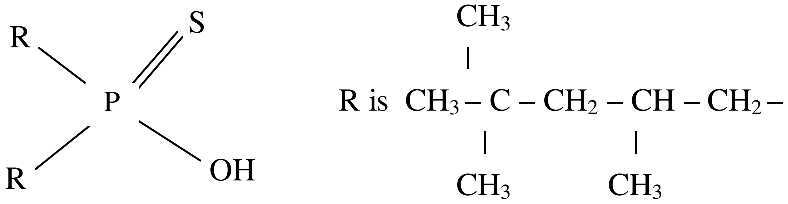


Fig. 3.3 Di (2, 4, 4,) trimethylpentyl monothiophosphinic acid (CYANEX 302)

PC 88 A®

PC 88A generically (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) (assay 95 % minimum by weight) produced by Daihachi Chemical Industry, Japan was generously supplied by Rubamin Chemicals Pvt. Ltd. Baroda. This extractant is a phosphonic derivative and finds wide application in the refining of rare earth metals and can also be used as an extractant for extraction of other metals such as zinc, cobalt, nickel etc.

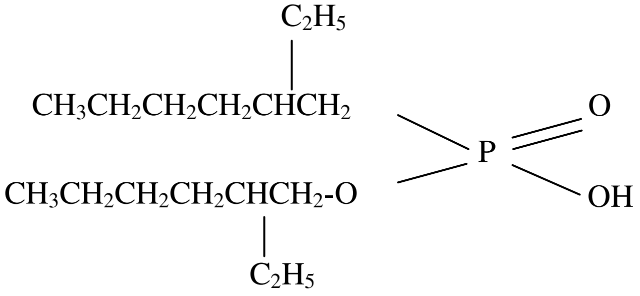


Fig. 3.4.: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC 88A)

Physical data: Molecular formula: $(C_8H_{17})_2HPO_3$, Molecular weight: 306.4, Appearance: colorless to light yellowish liquid, Texture: oily, Odor: odorless, Flash point: 170±3 °C, Lighting point: 203 °C, Solidifying point: - 47 °C, Density at 25 °C:~ 0.94 – 0.96 gm/ml, Viscosity: 36±3 mPa s, refractive index: 1.4480 – 1.4520.

LIX 84-I®

LIX 84 I chemically known as 2-hydroxy-5 nonylacetophenone oxime was supplied by Cognis Inc. Ireland. LIX 84 I is a water soluble ketoxime. It is a commercial extractant used in copper hydrometallurgy. It can function with acid and ammoniacal leach solutions and is more selective than other extractant classes. Although kinetically slower than ion pair extractants, LIX 84 I has good physical properties in terms of phase separation, low aqueous solubility, and chemical stability.

Physical data: Appearance: Fluid amber liquid, Texture: oily, Odor: of mineral oil, Flash point: > 160 °F, approximate density at 25 °C: 0.90 - 0.91 g/cm^3, Viscosity (kinematic) at 40 °C: 2.71 mPa/s

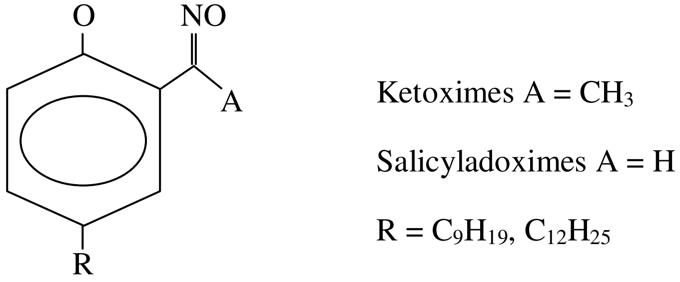


Fig. 3.5 2-hydroxy-5 nonylacetophenone oxime (LIX 84I)

3.1.2 Metal Solutes

Extraction studies were carried out in sulphate media and ammoniacal media. The metals salts and the ancillary reagents and chemicals used in this study are listed below:-

- Cupric Sulphate ($CuSO_45H_2O$) of excelar grade having 99.5% purity supplied by Qualigens was the copper source.
- Nickel sulphate ($NiSO_46H_2O$) having assay of 23% nickel supplied by Ranbaxy laboratories Ltd. was the nickel source
- Zinc Sulphate ($ZnSO_47H_2O$) of excelar grade having minimum 99.5 % purity supplied by Merck Specialties Pvt. Ltd. was the zinc source.

3.1.3 Ancillary reagents and chemicals

Sulfuric acid of AR grade with assay 98% was of Ranbaxy make

Sodium Hydroxide with assay 98% was of Ranbaxy make.

Ammonium Solution (25%) having specific gravity 0.91 was of Ranbaxy make

Standard pH buffer of 4 pH, 7 pH and 9.2 pH of Qualigens make were used.

Certified Atomic absorption spectroscopy standards of SRL make were used to generate standard curves for metal analysis.

3.2 Emulsion Liquid Membrane Formulation

The W/O emulsions were formulated by mixing the membrane phase and the aqueous stripping phase (sulfuric acid, concentration ranging from 0.5 M – 1.5 M), using a high speed blender at 12,000 rpm. The oil membrane phase of the emulsions was primarily kerosene (membrane material) which was mixed with the emulsifier Span 80 and the carrier such as D_2EHPA, PC88A, LIX 84I etc. In most cases Span 80 concentration was 3 % wt of the membrane phase while the carrier concentrations ranged from 2 - 20 % volume of the membrane phase.

The emulsion was prepared in a 600-ml long form beaker kept in a chilled water bath so as to dissipate the heat liberated due to intense mixing. Good emulsion formulation practices suggest that on a laboratory scale intermittent mixing is favorable for stable emulsion formulation. Hence, blending was carried out with pause at regular time intervals. The total time for emulsification was 450 seconds. The emulsions obtained were of milky white color and largely stable during the course of extraction experimentations. The emulsion prepared was not immediately used but was allowed to cure for thirty minutes so that internal morphological rearrangements could take place resulting in a more stable emulsion.

Emulsions were prepared with fixed volumes of membrane phase and inner phase. Usually volume ratio of one was opted however, to enhance the stoichiometric capacity of the internal stripping phase of the emulsion without altering the concentration of the internal reagent phase, the internal phase volumes were varied in such a manner that the internal phase volume fraction (ϕ) of the emulsions ranged from 0.5 to 0.64.

3.3 Emulsion Characterization

The water in oil (W/O) emulsion is the key constituent in the ELM process necessitating characterization of these emulsions. The W/O emulsions prepared in this investigation were characterized based on density, viscosity, interfacial tension, internal droplet sizes and stability.

Densities of the emulsions were measured using a certified density bottle at the temperature of extraction. Viscosities of the emulsion were measured using Brookfield Cone and Plate Rheometer model LVDV III+CP using CPE 52 cone spindle. The cone angle was 3 degree, the spindle radius was 1.2 cm and the sample volume used was 0.5ml. Since LVDV-III + rheometer has the flexibility to operate at variable speeds, viscosity data could be conveniently obtained at varying shear rates. The viscosity data was collected in the direction of increasing shear rates over a wide range of shear rates to quantify the rheological behavior of emulsions.

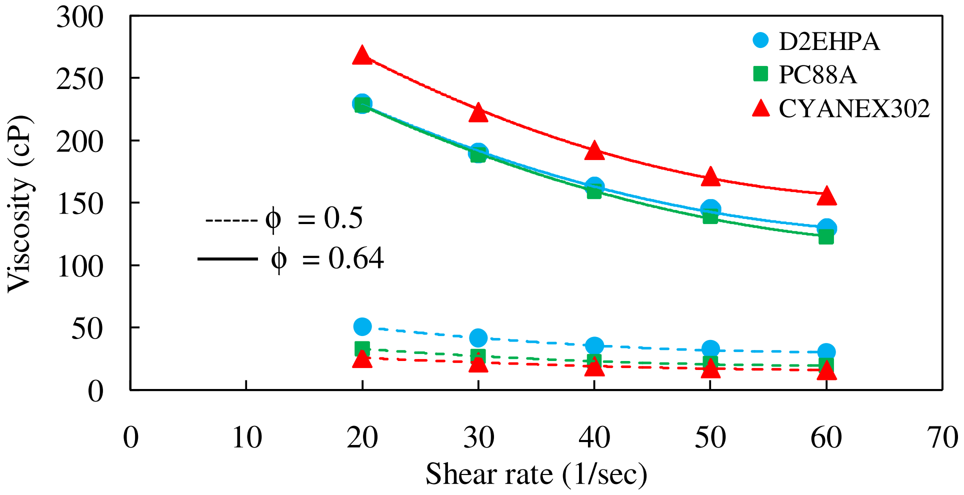


Fig.3.6: Effect of shear rate on viscosity of emulsion

Figure 3.6 shows the effect of shear rate on the viscosity of the emulsions prepared using the three organophosphorous acids (having Cc = 10% v/v, surfactant concentration 3%wt of oil phase and internal phase acid concentration 1.5M) at volume fractions of 0.5 and 0.64. It is observed the viscosities were very sensitive to the internal phase volume fraction. At $\phi = 0.5$, D2EHPA emulsions are more viscous at all shear rates in comparison to the emulsions with PC 88A and Cyanex 302, but as ϕ is increased to 0.64 the Cyanex 302 emulsion become much more viscous than the emulsions with D2EHPA and PC 88A. The viscosity of

D2EHPA and PC 88A at $\phi = 0.64$ were identical such similarity was observed in the viscosities of PC 88A and Cyanex 302 at $\phi = 0.5$. In the range of shear rates studied the emulsions showed shear thinning behavior and obeyed the power law model.

Internal drop size of the emulsion, a very important characterization parameter, was determined microscopically by Olympus microscope model BH-2 attached with a Olympus photo micrographic system model PM-10 AD. A small volume of emulsion was diluted 15 times in an appropriate solvent (kerosene or liquid paraffin). A drop of diluted emulsion was placed in the center of the slide and covered with a cover slip. Internal drop sizes were measured quickly using an ocular and stage micrometer (Erma make) at magnification of 600 X and 1500 X. more than 300 droplet sizes per slide were counted.

To ensure greater accuracy two slide's were prepared for each emulsion based on the total data of more than 600 measurements the average value of d_{32} was calculated for each case. Photomicrography of the internal droplets of the emulsion was carried out using the Olympus photomicrography system model PM-10AD attached with an exposure control unit to the microscope at magnifications of 600 X.

The interfacial tension between the emulsion phase and the solute containing aqueous phase was measured using Du Nuoy tensiometer using a ring made up of platinum – iridium. Ring method allows interfacial tension readings to be made in very short time period of 15-30 seconds with reproduced accuracy within $\pm$ 0.05 dyne/cm. Table 3.1 lists the effect of the carrier concentration on the emulsion characterization parameters.

Table 3.1: Effect of D2EHPA concentration (Cc) on viscosity, interfacial tension between emulsion and feed phase, density and internal drop size of emulsions.

Parameter measured (Emulsion formulated with W_{surf}=3wt%, ϕ=0.5, Cio=1.5 M and Ceo=1000 mg/L of zinc).	Variation in carrier (D2EHPA) concentration % (v/v)			
	0 %	2 %	5 %	10 %
Viscosity at 20 s^{-1} (μ) – cP	30.38	31.33	34.55	50.68
Interfacial Tension (γ) – mN/m	14.1	10.3	6.5	4.2
Density (ρ) - kg/m^3	903.6	953.0	958.0	967.3
Internal drop size - μm	5.13	5.54	5.58	5.65

3.4 Experimental Set up and Extraction methodology

The experimental set-up consisted of a four baffled stirred vessel 0.105 m diameter having 1000-ml (1 liter) capacity that functioned as a batch reactor. The agitator assembly consisted of a single phase variable speed 1 / 12 hp motor of Remi make, model no. RU-56-2G. The motor speed was regulated using a dimerstat and its speed under actual operating conditions was measured using a *Jaquet* make tachometer. The projected view of reaction vessel is shown in Fig. 3.7, the impeller used was a six blade disk turbine having dimensions as shown in Fig. 3.8.

Ammoniacal feed solution for extraction was prepared by dissolving metal sulphate (copper, zinc and nickel) and ammonium sulphate (50 g/L) in deionised water. The feed pH was adjusted to the desired value using ammonium hydroxide. Feed solutions for zinc extraction using organophosphorous acids were prepared by precisely weighing and dissolving the necessary amount of zinc in deionised water. The pH of the feed was adjusted using H_2SO_4 or Na_2CO_3. These feed solutions were charged to the extractor that filled the extractor up to a height of 7.5 cm from the bottom. The impeller was positioned at a distance of 4.5 cm from the bottom and then the agitation was started at a constant rate.

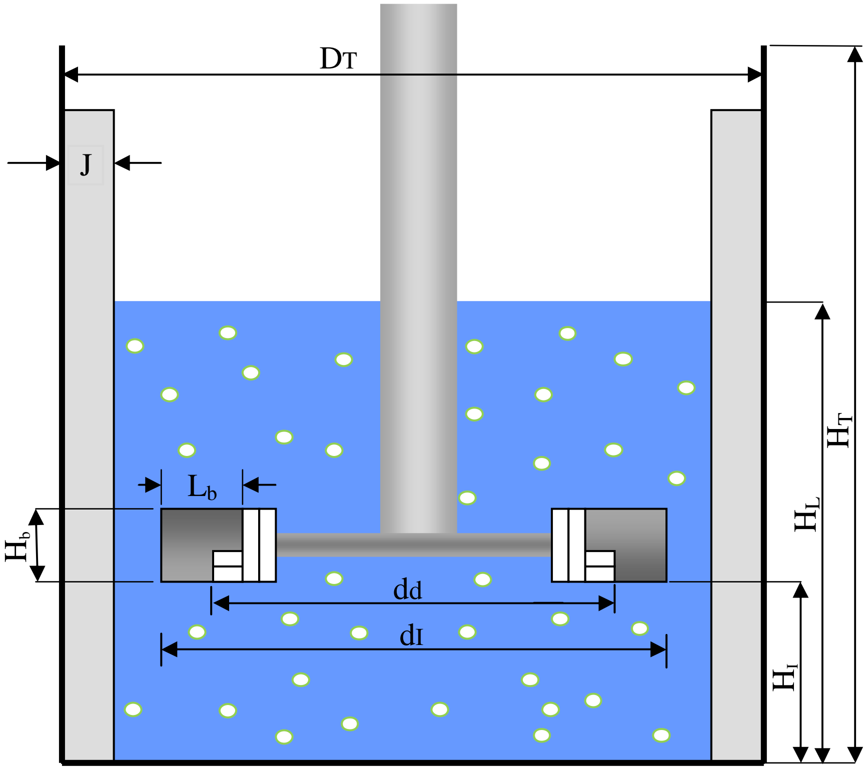
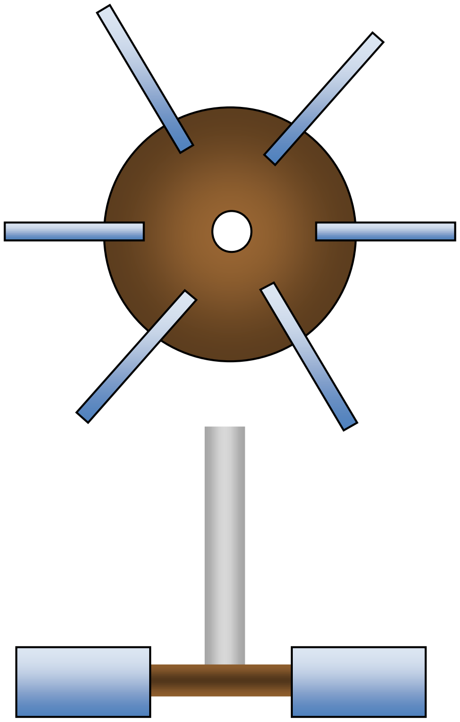


Fig. 3.7 Projected views of impeller and reaction vessel

The cured W/O emulsion was quickly poured in the extractor in necessary amount to get the desired emulsion to feed ratio (Treat ratio). As soon as the emulsion was poured in the agitated feed phase it got dispersed in the form of fine globules 1 to 3 mm in diameter within ~ 30 seconds. Samples of the aqueous phase were withdrawn at specific time intervals without stopping the agitation. Since sampling was carried out from continuous phase, where the emulsion was finely dispersed, it was necessary to plug the tip of the sampler so that the movement of emulsion globules was inhibited and only the aqueous phase was sampled.



Element	**Type/ Size (m)**
Internal Diameter	0.105
Height (HT)	0.14
Liquid Height (HL)	0.076
Impeller Diameter(dI)	0.052
Disk Diameter (dd)	0.038
Type of Impeller	Flat Blade Turbine
No. of Blades on the Impeller	6
Blade Height (Hb)	0.010
Length of blade (Lb)	0.045
Height of the impeller off bottom (HI)	0.013
Baffle width (J)	0.008

Fig. 3.8 Six bladed turbine impeller and its dimensions

Batch extraction runs were carried out for fixed period of time that extended from 3 to 10 minutes. The extraction runs were carried out at temperatures 30±1^{0}C. On completion of the extraction run duration the agitation was stopped, this resulted in rapid separation of the emulsion phase from the aqueous phase. The total contents of the extractor were poured in a separating funnel and the emulsion phase was separated from the aqueous phase. The final volume of the emulsion phase was measured to get an estimate of emulsion swelling due to water transport. The samples collected during the experimental run were then analyzed for the metal content after necessary dilutions using an atomic absorption spectrophotometer. Extraction data were plotted as ratio of instantaneous metal concentration to initial concentration (Ce/Ceo) versus time.

3.5 Analysis of Metals

The metal ion concentrations were measured using an atomic absorption spectrophotometer (Chemito Make Model AA- 203) equipped with Photon make hollow cathode lamps for copper, nickel and zinc. The instrument was fully computer controlled using software AA203 data station version 3.2. The optimized instrument parameters for measurement of targeted metal ions are given in Table 3.2.

Table 3.2 Optimized instrument parameters for measurement of targeted metal ions

Parameter	Copper	Nickel	Zinc
Wavelength (nm)	324.8	232.10	212.5
Current (mA)	5.0	9.0	5.0
Slit Width (nm)	0.5	0.3	1.0
Pmt (V)	274.7	370.7	333
Burner height (mm)	1.0	1.0	0.5
Fuel (liter/min)	3.5	3.55	3.5
Working range (ppm)	2 – 8	2 – 10	0 – 2

Ratio method was preferred for curve fitting. The samples of the experimental runs were appropriately diluted so that they were in the specified working range for the corresponding metals the concentrations were reported in ppm.

3.6 Other Parametric Measurements

3.6.1 pH measurement

Metal extractions studied in this work are extremely pH sensitive, particularly so with the proprietary carriers/ extractants that were used in this study. The pH measurements were made using a *Systronics* make digital pH meter that was calibrated at pH values of 4 and 7 for extraction of metal solutes from acidic media and pH of 9.2 for extraction of metal solutes from ammoniacal media using standard buffer solutions.

3.6.2 Swelling of emulsion

Swelling is the increase in volume of emulsion due to transport of water from continuous phase to dispersed emulsion phase. Swelling has a bearing on emulsion breakage and is an important design parameter. Swelling of emulsion was determined at the end of each extraction run by separating out the emulsion phase from the water phase and noting the change in volume of emulsion with respect to its initial volume.

3.6.3 IR Spectra

Fourier-Transform Infrared spectroscopy (FT-IR) is a useful tool to study the nature of groups present in a system. The nature of groups present, the bonding of the various groups in the extractant with the metal, the interaction between the extractant and the diluents etc. all get revealed by IR spectroscopy.

Heavy metals such as Cu, Zn, Ni and their mixtures form complexes of different nature with various metal extractants which can be revealed by FTIR spectroscopy. FTIR spectra of LIX 84I complexes with Cu, Zn and Cu+Zn were acquired using a Thermo Nicolet 6700 FT-IR spectrometer and D2EHPA, PC 88A, CYANEX 302 complexes with zinc were acquired using a Shimadzu FTIR spectrometer Model no. 8400S.

CHAPTER 4
EXTRACTION OF HEAVY METALS FROM AMMONIACAL SOLUTIONS

4.1 Introduction

In the last 50 years, there has been an upsurge of interest in the ammonia leaching process as a means of recovering zinc, copper, nickel and many other heavy metals from difficult or intractable feed stocks such as feeds having basic gangues (Wang *et al.* 2008); low-grade feeds or tailings where flotation and other means of separation have had limited success (Buckett *et al.* 1998); zinc-containing waste from galvanizing operations (Kasai *et al.* 1987, Lozano Blanco *et al.* 1999); zinc containing dust that is given off during steelmaking (Dreisinger *et al.* 1990, Nyirenda and Lugtmeijer 1993); and the etching of copper from printed circuit boards using ammonium chloride and ammonium sulphate.

Ammonia is an attractive lixiviant due to its high complexation characteristics with heavy metals, low toxicity, low cost and ease of regeneration by evaporation. Furthermore, the major waste components in ores, such as Fe_2O_3, SiO_2, CaO and MgO are insoluble in ammoniacal solutions which allow selective extraction of different heavy metals; zinc, copper, nickel, cadmium etc. using solvent extraction from ammoniacal solutions.

Solvent extraction is the preferred technique for separating and enriching the desired metal values from ammoniacal solutions. It offers numerous advantages such as absence of sludge formation, greater ease and flexibility of operations, ability to handle wide range of feed concentrations, choice of solvents to control selectivity of separation etc. Extraction of copper, individually or with other metal values from ammonium carbonate or ammonium sulphate leach liquors has been investigated by several investigators.

β-diketones are a versatile class of chelating agents employed for the analytical separation of metal ions from ammoniacal media. There are several other extractants for example: the LIX type of reagents; SME 529; Hostarex DK16; and LIX 54; used for extracting various heavy metals from ammoniacal solutions. LIX 87QN used for extraction of nickel has been specially developed for this purpose and has been tested for nickel extraction from ammoniacal carbonate solutions and stripping at higher concentrations of ammonium carbonate. This extraction and stripping operation results in highly pure nickel carbonate solution suitable for the preparation of basic nickel carbonate / nickel oxide.

The commercial reagent LIX 54 extracts copper from ammoniacal leaching solutions and offers some advantages including low loading of ammonia and ease of stripping and faster kinetics (Gameiro *et al.* 2008). Alguacil and Alonso (1999) have studied the extraction of zinc from ammonium sulphate solutions using LIX 54 whilst Rao *et al.* (1992) carried out a similar investigation with Hostarex DK-16 a commercial reagent similar to LIX 54. Unexpectedly, it was found at the Escondida plant that LIX 54 reacts with ammonia to give surface active molecules that appear to increase the entrainment of aqueous phase in the loaded organic phase resulting in carryover of ammonia to the wash stage and consequently a decrease in the copper stripping kinetics (Kordosky *et al.* 1999). To overcome this problem, Cognis designed several sterically hindered extractant molecules, called XI-55 and XI-57, which do not react with ammonia in the manner of LIX 54 (Kordosky *et al.* 2002). However, compared with copper, zinc is relatively difficult to recover from its ammoniacal solutions using β-diketone extractants (Przeszlakowskia and Wydr 1982).

The advent of the electronic industry has led to an increased generation of printed circuit boards for use in various electronic devices. The printed circuit boards after their life cycle become a major component of electronic wastes from which heavy metals such as copper, zinc, silver etc. can be effectively recovered and reclaimed. The recovery procedure involves leaching out the metal values from the wastes which is most effectively done using ammonia as the leachant. The metal values can be subsequently extracted using solvent extraction. However, the ELM technique can very well be justifiable in this case for reasons such as reduction of the solvent inventory, enhancement of the rate and capacity of the process leading to rapid processing and smaller plant sizes. Alguacil (2001) was the first to study the permeation of copper from a feed of ammoniacal-ammonium carbonate solution through a supported liquid membrane impregnated with LIX 973N. Recently Gameiro *et al.* (2007) have reported the extraction of copper from ammoniacal solution using ELMs with LIX 54 as carrier.

Nickel-bearing ores or concentrates such as laterites are usually processed using hydrometallurgical techniques involving reduction roasting followed by ammoniacal leaching to bring the metal values into solution as their ammine complexes. Due to the very low concentration of nickel in these ores and also due to the presence of other metals, such as cobalt and copper, the leach liquors are lean and impure. In this case too there is considerable scope to extract these metals selectively from their ammoniacal leachate solutions into ELMs, thereby recovering and concentrating them.

The objective of this investigation was to determine the efficacy of the ELM technique for metal extraction from ammoniacal solutions using commercially available metal extractants as carrier. The scope of the investigation was to explore the removal of transition metal cations such as Cu, Zn and Ni from ammoniacal solutions independently as well as from binary solutions of these metals using LIX 84I.

4.2 Copper extraction from ammoniacal solutions

It is well known that leach liquors arising from ammoniacal leaching contain metals as their ammine complex $M(NH3)_4^{2+}$. Extraction of copper from ammoniacal solutions using LIX 84I can be described by the following chemical reaction:

$$[Cu(NH_3)_4]_{aq}^{2+} + 2RH_{org} \leftrightarrow CuR_{2org} + 2NH_4{}^{+}{}_{aq} + 2NH_{3aq} \qquad \ldots\ldots(4.1)$$

Eq. (4.1) shows that after extraction there is an increase in the ammonia concentration in the aqueous phase due to release of ammonia bonded to metal ions leading to an increase in pH. Bhaskara Sarma and Nathsarma (1993) have reported that in actual practice often there is no increase in pH due to buffering by ammonium ion, rather a small decrease due to take up of ammonia by the solvent. They also observed that copper extraction remains steady up to pH 8, but beyond this, copper extraction decreases slowly up to pH 10.5 and sharply at pH 10.9.

Lee and Chan (1990) extracted ammonia from dilute solutions into ELMs and they reported the effect of pH on molecular ammonia–ammonium ion shift. Since NH_4^+ ion is not soluble in the oil membrane, only free ammonia can be transported and trapped within the membrane and this requires the pH to be adjusted ≥ 12. These investigators observed that at pH 9.5, free ammonia content is only 50%; while at pH 8 it is less than 10%. In view of these findings the effect of pH was first investigated to establish optimal operating conditions for copper removal from ammoniacal-ammonium sulphate solutions.

4.2.1 Solvent extraction and stripping behavior of copper from ammoniacal solutions

In ELM systems loading and stripping occur simultaneously. To assess the relative influence of loading and stripping phenomena equilibration and stripping studies were conducted separately. Loading of copper from ammoniacal-ammonium sulphate solutions were carried out by equilibrating equal volumes of the aqueous solution at pH 8.1 with kerosene containing LIX 84I.

Copper loading was observed to be instantaneous and quantitative in the three equilibration studies carried out at LIX 84I concentration of 2% (v/v), 5% (v/v) and 10% (v/v) in the oil phase. Stripping of loaded organic phase with 1.5 M H_2SO_4 under identical well-agitated conditions revealed that in one minute contact copper stripped better from oil phase containing 5% (v/v) LIX 84I in comparison with the other two cases as seen in Fig. 4.1. However, as time of contact increased copper stripped better from the oil phase containing 10% (v/v) LIX 84I. Faster stripping rates augment the overall extraction rates in ELMs by making more amount of monomeric oxime available for loading.

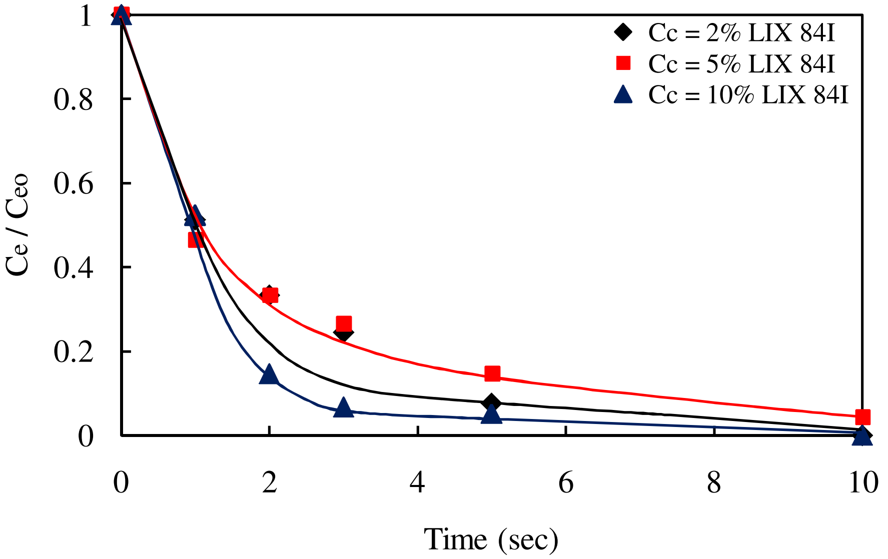


Fig. 4.1: Effect of carrier concentration on stripping of copper from loaded organic phase with strippant concentration=1.5 M.

The data reported in Fig. 4.1 may not directly reflect the true behavior of ELMs in view of the fact that the stripping phase in ELM are stationary and not well agitated and the stripping surface area obtained in ELMs are almost 3 to 4 orders of magnitude larger than obtained in stirred vessels. Nevertheless it provides a qualitative idea of the extraction pattern.

4.3 Copper extraction from ammoniacal solutions into ELMs

The extraction of solutes from aqueous solution into the W/O emulsions is affected by a number of process parameters which be broadly classified into two groups, the first group involves the factors influencing emulsion behavior and may be named emulsion parameters they include the carrier concentration, emulsifier concentration, volume fraction of the aqueous stripping phase in the W/O emulsion, stripping acid concentration in the internal phase. The second group is the set of operational parameters such as pH, speed of agitation, initial feed concentration, treat ratio i.e. the ratio of emulsion phase to feed phase, these are not directly affected by emulsion properties but can be indirectly influenced by the nature of emulsion.

Pilot experiments revealed that W/O emulsions could be adequately dispersed in the feed by stirring at 160 rpm. Lower stirring rates failed to disperse the emulsion adequately leaving a film of emulsion on the surface of the feed phase. On the other hand, higher stirring rates of 190 rpm gave a very fine dispersion of the emulsion that increased extraction rates but caused significant emulsion breakage. It was also found that emulsions formulated with 3 wt% surfactant concentration in the membrane phase were adequate for membrane stability. Increasing surfactant concentration to 5 wt% did not have any significant effect on the extraction rates, nor did it enhance the membrane stability; but reducing the surfactant concentration to 2 wt% caused the emulsion to disintegrate very rapidly when dispersed in the feed. All investigations were subsequently performed using emulsions formulated with 3 wt% Span 80 in the membrane phase and the emulsions were dispersed in the feed at 160 rpm.

Once the emulsifier concentration and the speed of agitation was fixed, effect of other process variables were investigated for the extraction of copper from ammoniacal solutions using ELMs containing LIX 84I as the carrier. The effect of pH which has a key bearing on all metal extractions was first investigated and thereafter the effect of emulsion parameters were explored and after that the other operational parameters were investigated. The results are detailed below:

4.3.1 Effect of pH

The effect of feed phase pH on extraction was studied at pH 8.1 and pH 9.1. Emulsions used were formulated with equal volume of kerosene and stripping phases giving the internal phase volume fraction ϕ=0.5, carrier concentration Cc=10% (v/v) LIX 84I, and the internal phase sulfuric acid concentration Cio=1.5 M. The initial feed concentration was Ceo≈ 500 mg/L and the treat ratio (TR) of the emulsion to the feed was maintained at 1:6.

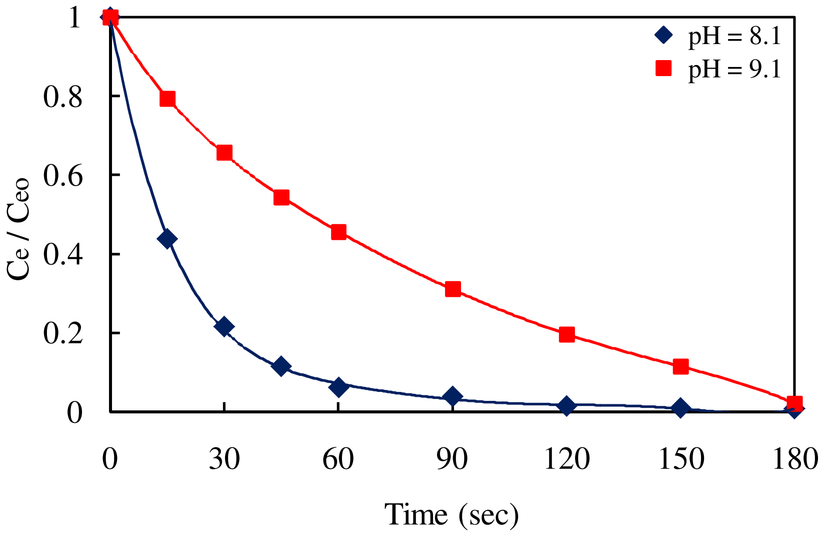


Fig. 4.2: Effect of feed pH on rate of copper extraction
(ϕ=0.5, W_{surf} =3 wt%, Cio=1.5 M, Cc=10% (v/v), Ceo≈ 500 mg/L, TR=1: 6, N=160 rpm).

Fig. 4.2 shows that the rate of extraction of copper from ammoniacal-ammonium sulphate solutions is very rapid. Quantitative extraction of copper was observed at both pH values but the rate of extraction at pH 8.1 was considerably faster than at pH 9.1. For further investigations the feed phase pH was fixed at pH 8.1, which ensured that free ammonia transport across the membrane was minimal. It was observed that in just 2 min duration quantitative extraction of copper occurred at pH 8.1; hence, extraction runs were carried out for 3 min in most cases. In this short duration of extraction runs there was no evidence of membrane breakage or rupture.

4.3.2 Effect of carrier concentration (Cc)

Carrier concentration in the membrane phase has considerable influence on the overall extraction rates in ELMs. Sengupta *et al.* (2006) observed an increase in copper extraction rates with an increase in LIX 84I concentration in the membrane phase up to 10% (v/v) but further increase in LIX 84I concentration to 15% (v/v) and 20% (v/v) led to a decline in the rates of extraction. Decline in extraction rates with an increase in oxime concentration in membranes could be due to the tendency of oximes to form aggregates at high concentrations. Oxime aggregates have less surface activity than monomers and tend to stay away from the surface that leads to non-availability of oxime for chelation at the feed – membrane interface (Whewell and Hanson 1981).

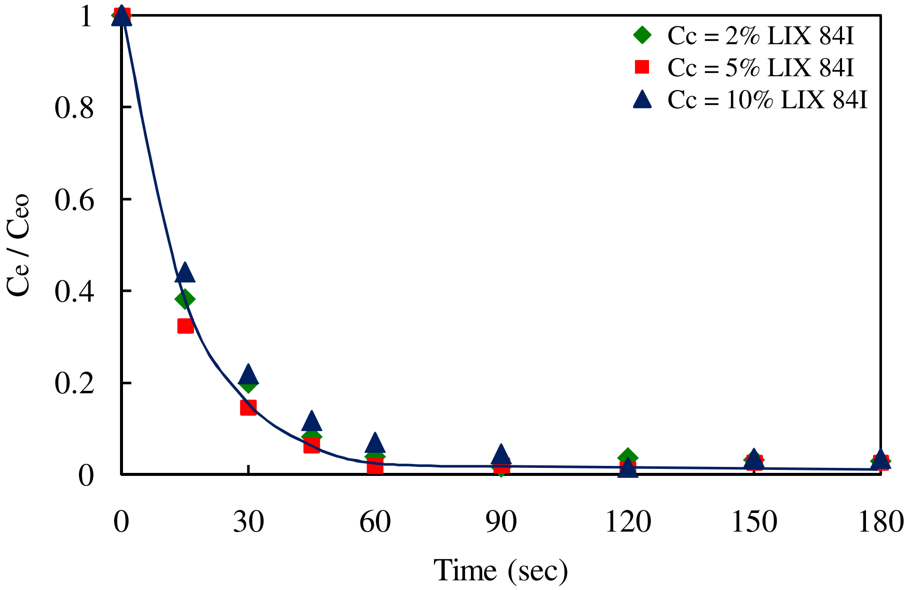


Fig. 4.3: Effect of carrier concentration on rate of copper extraction
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, pH=8.1, Ceo≈ 500 mg/L, TR=1: 6, N=160 rpm).

A consequence of this effect is an increase in the interfacial tension between the membrane and feed phase with an increase in the oxime concentration in the membrane as observed by Takashashi and Takeuchi (1986). Inoue *et al.* (1986) investigated the interfacial equilibria of hydroxime copper chelates, they observed that the surface activity of the copper chelates CuR_2 was lower than that of the oxime. Moreover, a decrease in the total oxime concentration occurs in the oil phase as extraction proceeds since two molecules of oxime chelates with copper to turn into one molecule of CuR_2 by reaction. As a consequence of this, interfacial tensions increase as copper loading increases.

Effect of carrier concentration on copper extraction was investigated at three LIX 84I concentrations in the membrane phase ranging from 2% (v/v) to 10% (v/v) using emulsions having ϕ=0.5 and Cio=1.5 M H_2SO_4. The treat ratio was maintained at 1: 6 and initial copper concentration Ceo was nearly 500 mg/L. For all three cases about 97% copper was extracted in three minutes contact. The extraction rates did not differ significantly, as can be observed from Fig. 4.3, but in the first 60 s extraction rates for 10% (v/v) oxime concentration were lower than that observed for 2% (v/v) and 5% (v/v) oxime concentrations. Extraction rates were found to be highest with 5% (v/v) oxime concentration in the membrane phase.

Another factor contributing to variation in extraction rates with change in extractant concentration is the interfacial tension between membrane and feed phase. Interfacial tensions increased with an increase in LIX 84I concentration in the membrane phase leading to formation of larger sized emulsion globules in the dispersed emulsion under otherwise identical conditions. It was observed that emulsions containing 10% (v/v) LIX 84I in the membrane resulted in globule sizes having Sauter mean diameter d_{32}=0:436 mm while emulsions having 5% (v/v) LIX 84I gave globules having d_{32}=0.406 mm. Formation of larger size globules do not influence the copper loading rates but the copper-oxime complex formed at feed-membrane interface has to diffuse greater distance within the globule to get stripped when compared with small size globules formed with low interfacial tension systems. This effect could manifest in relatively lower rates in short contact times as observed in Fig. 4.3

Interfacial tension between the feed and emulsion phase was determined using Du-Nuoy ring method. Interfacial tensions for emulsions containing 2% (v/v), 5% (v/v) and 10% (v/v) LIX 84I were 6.2 mN/m, 8.7 mN/m and 11 mN/m respectively. Increase in interfacial tensions as well as the decline in extraction rates with corresponding increase in LIX 84I concentration in the emulsion phase could be attributed to increased copper loading at higher LIX 84I concentrations.

4.3.3 Effect of internal phase acid concentration (Cio)

The internal phase acid concentration was varied to study the influence of stripping on overall extraction rates. Extractions were performed with varying H_2SO_4 concentrations (0.5 M, 1.0 M and 1.5 M) in the internal emulsion phase to study the effect of Cio on extraction rates. Taking a clue from Fig. 4.1 that shows the stripping process to be influenced by the carrier concentration, the effect of Cio was investigated at two different carrier concentrations 5% (v/v) and 10% (v/v) LIX 84I respectively using emulsions having ϕ=0.5 with treat ratio of 1:6 and Ceo$\approx$ 500 mg/L copper.

Fig. 4.4 shows the effect of Cio on extraction rates when LIX 84I concentration in the membrane phase was 10% (v/v). Within 2 minutes time quantitative copper removal was observed in all three cases. Extraction using emulsions having Cio=1.5 M H_2SO_4 where more gradual in the first two minutes, in comparison to copper extraction using emulsions with Cio 1.0 M and 0.5 M, which were more rapid.

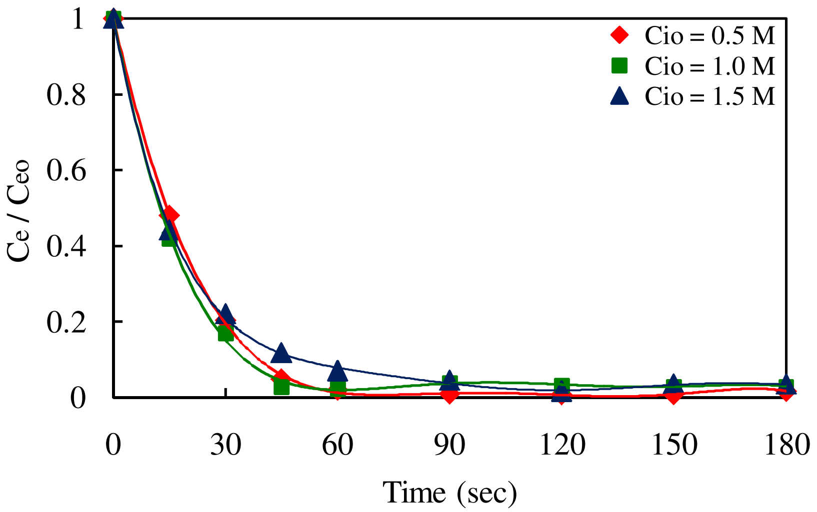


Fig. 4.4: Effect of internal phase acid concentration on rate of copper extraction using 10% (v/v) LIX 84I

(ϕ=0.5, W_{surf}=3 wt%, Cc=10% (v/v), pH=8.1, Ceo≈ 500 mg/L, TR=1: 6, N=160 rpm).

When LIX 84I concentration in the membrane was 5% (v/v), the effect of Cio on the extraction rates are shown in Fig. 4.5. It is observed that increasing Cio leads to considerable increase in the copper extraction rates. The difference in the extraction behavior observed in Figs. 4.4 and 4.5 stems from two facts: 1) reduction of LIX 84I concentration from 10% (v/v) to 5% (v/v) reduces the loading capacity of the oil membrane by half, 2) there is a threefold change in the capacity of the acid to strip copper in the range of Cio investigated (although the stripping rates may not be very different with varying acid concentrations during the short time span of the experiment).

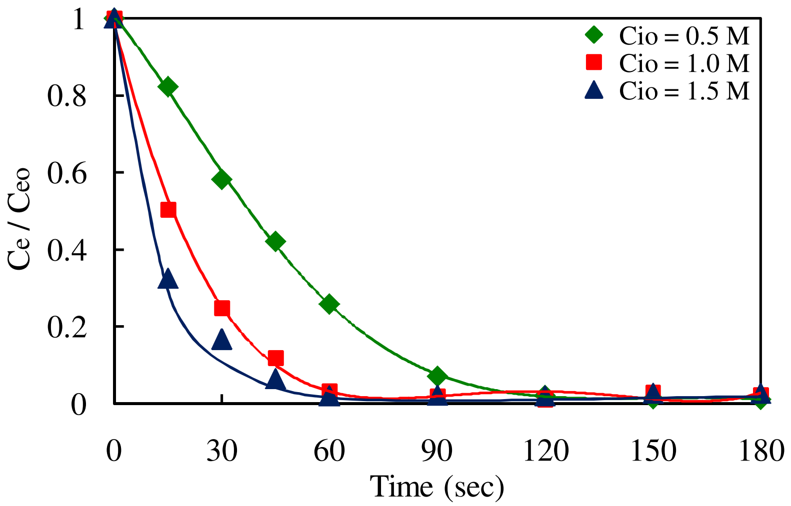


Fig. 4.5: Effect of internal phase acid concentration on rate of copper extraction using 5% (v/v) LIX 84I

(ϕ=0.5, W_{surf}=3 wt%, Cc=5% (v/v), pH=8.1, Ceo≈ 500 mg/L, TR=1: 6, N=160 rpm).

4.3.4 Effect of internal phase volume fraction (ϕ)

Changes in the internal phase volume fraction of emulsion result in a change in the emulsion morphology. All sensible properties of emulsion increase with an increase in ϕ. An increase in ϕ leads to an increase in the overall capacity of the membrane due to an increase in the amount of stripping phase in the emulsion. Increase in ϕ is analogous to formation of thinner membranes that causes a decrease in the diffusional resistance. Hence, it is expected that increase in ϕ would also lead to faster extraction rates. Effect of variation of ϕ was investigated for emulsions having ϕ=0.5 and ϕ=0.64. The emulsions were formulated with 5% (v/v) LIX 84I in the membrane phase and dispersed in feed containing 928 mg/L copper. The treat ratio was maintained 1:6. The extraction curves are plotted in Fig. 4.6.

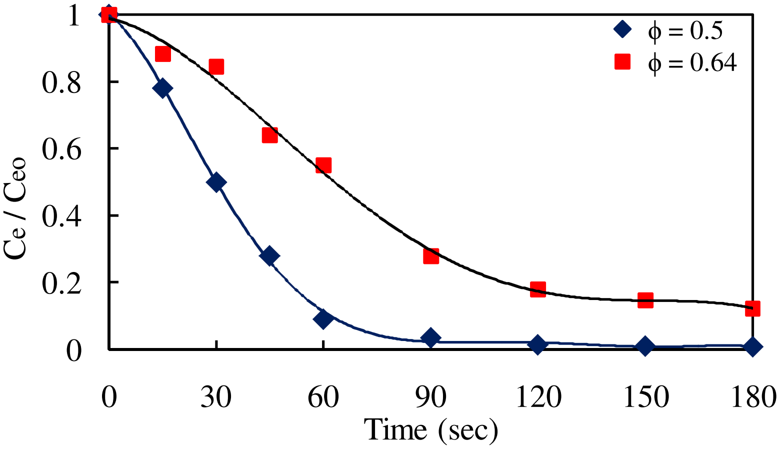


Fig. 4.6: Effect of internal phase volume fraction on rate of copper extraction (W_{surf}=3 wt%, Cio=1.5 M, Cc=5% (v/v), pH=8.1, Ceo=928 mg/L, TR=1: 6, N=160 rpm).

The results appear to be contrary to the expectations with both extent of removal as well as rate of removal being less when ϕ is larger. The extraction behavior observed could again be attributed to the rapid loading of copper from ammoniacal sulphate solutions in ELMs containing LIX 84I in the membrane phase. Increase in ϕ while maintaining treat ratio 1:6 resulted in decrease of the oil membrane phase of the emulsion and also in the amount of the carrier. Hence, there was a significant decrease in the copper take up by the membrane phase. This effect was augmented by a large increase in the inner phase droplet sizes of the emulsion when ϕ was 0.64.

Fig. 4.7 shows the inner drop size distributions of the emulsions used. There is a considerable shift in the drop size distribution towards larger sizes with emulsions having ϕ=0.64, the

Sauter mean diameter d_{32} of the emulsion having ϕ=0.5 and ϕ=0.64 turn out to be 2.72 and 10.75 μm respectively.

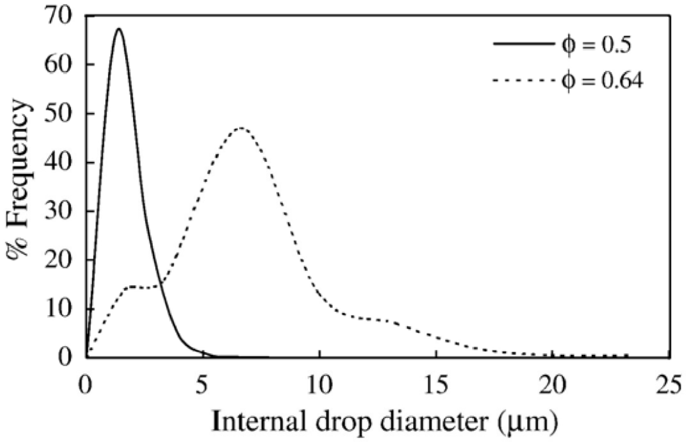


Fig. 4.7: Variation of internal drop size distribution with ϕ (W_{surf}=3 wt%, Cio=1.5 M, Cc=5% v/v).

Such large increase in internal drop sizes result in a substantial decrease in stripping surface area. This decrease is not compensated by the corresponding decrease in diffusional resistance expected when ϕ=0.64. Hence, a sharp decrease in the extraction rates is observed in Fig. 4.6.

4.3.5 Effect of initial feed concentration (Ceo)

The effect of Ceo on the rates of copper extraction was studied over a wide range of copper concentrations. The effect of Ceo variation augments the effect of Cc. It is expected that if Ceo is low and Cc is large then the loading capacity of the emulsion membrane phase would dominate the entire extraction process and mask the influence of the other physicochemical processes encountered in ELMs. The effect of Ceo was studied using emulsions containing 5% (v/v) as well as 10% (v/v) LIX 84I in the membrane phase. These emulsions were formulated with ϕ=0.5 and Cio=1.5 M. The treat ratio was maintained at 1:6. For emulsions containing 5% (v/v) LIX 84I in the membrane phase the extraction curves for feed concentrations of 500 mg/L, 928 mg/L and 1570 mg/L all diverge out due to a limitation in loading capacities of these emulsions, as shown in Fig. 4.8.

Quantitative extraction is observed in 60 s for Ceo=500 mg/L, 90 s for Ceo=928 mg/L; but for Ceo=1570 mg/L only 85% extraction was observed in 180 s of contact. The loading of copper from ammoniacal solutions in the membrane is very fast, but the extent of loading depends on the amount of carrier present. If sufficient amount of carrier is present, then loading tends to

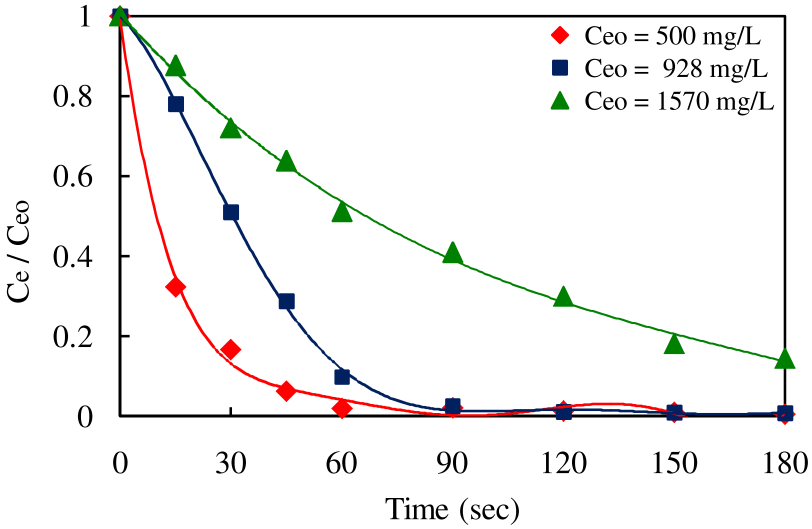


Fig. 4.8: Effect of initial feed concentration on rate of copper extraction using 5% (v/v) LIX 84I

(ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, Cc=5% (v/v), pH=8.1, TR=1: 6, N=160 rpm).

dictate the overall rates. Only when carrier concentration is limited other physico-chemical features like stripping rates, diffusion of the oxime, diffusion of oxime-copper complex, emulsion morphology etc. influence the overall extraction. The difference in rates of extraction observed in Fig. 4.8 is attributed to the requirement of the copper-oxime complex to diffuse deep within the emulsion globule to get stripped caused by the saturation of the internal phase droplets in the peripheral regions of the emulsion globules when Ceo is large.

Fig. 4.9 shows the effect of Ceo for emulsion containing 10% (v/v) LIX 84I in the membrane phase. Ceo was varied in the range of 497 mg/L to 3120 mg/L. The extraction curves for 497 mg/L and 1064 mg/L converge together after 60 s duration while the extraction curves for 1925 mg/L and 3120 mg/L diverge out. Since the copper loading capacities in the emulsions containing 10% (v/v) LIX 84I is quite large, up to Ceo=1064 mg/L, the extraction rates appear to be dominated by the loading rates. When Ceo is increased sharply, aspects like stripping, diffusion of the copper–oxime complex etc become increasingly important. In such situations loading alone is not sufficient to sustain the extraction rates as can be seen from the nature of extraction curves of 1925 mg/L and 3120 mg/L. In both these cases, 88% extraction is noted in 180 s.

The lack of similarity between the extraction curves obtained for case I: Ceo=928 mg/L, Cc=5% (v/v) LIX 84I in Fig. 4.8 and case II: Ceo=1925 mg/L, Cc=10% (v/v) LIX 84I in Fig. 4.9 is apparent. Although Ceo and Cc are double in case II in comparison with case I, even then the two curves do not show identity of scale. The difference in the nature of these extraction curves stem from the greater value of interfacial tension observed between the emulsion and feed phase for the emulsions containing 10% (v/v) LIX 84I in comparison with emulsions containing 5% (v/v) LIX 84I.

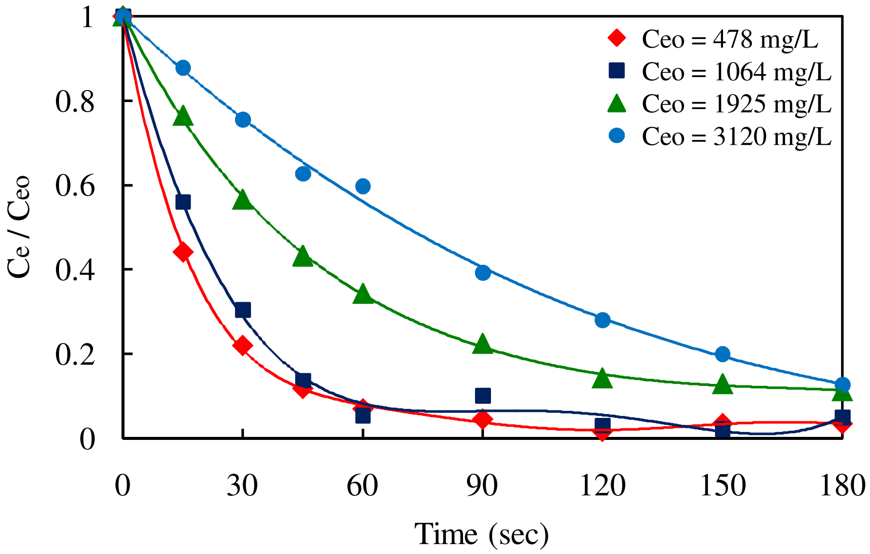


Fig. 4.9: Effect of initial feed concentration on rate of copper extraction using 10% (v/v) LIX 84I

(ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, Cc=10% (v/v), pH=8.1, TR=1: 6, N=160 rpm).

Lower interfacial tension results in formation of smaller globules under otherwise identical conditions as reported earlier in Section 4.3.2. Hence, for the same treat ratio it results in more globules formed, thereby generating larger contact area at the feed–membrane interface causing an increase in the rates of mass transfer. More importantly smaller sized globules also result in shorter diffusion path lengths that the oxime-copper complex has to travel within the globule to get stripped. Hence, if emulsion globules are smaller in size extraction will be more rapid as observed in case I.

4.3.6 Effect of treat ratio (TR)

Treat ratio is a measure of emulsion holdup in the system. An increase in treat ratio leads to an increase in emulsion holdup. It results in an increase in the overall extraction capacity of the emulsion due to increase in the amount of membrane phase and the stripping phase as well as the amount of carrier. An increase in treat ratio also results in an increase of the overall surface area of the system, it is therefore expected that increase in treat ratio would also result in increase in the copper extraction rates or vice-versa.

Extraction at treat ratios of 1: 6, 1:10 and 1:15 were performed using emulsions containing 10% (v/v) LIX 84I as carrier and having an internal phase fraction ϕ=0.5. The initial feed concentration was maintained at Ceo≈ 500 mg/L.

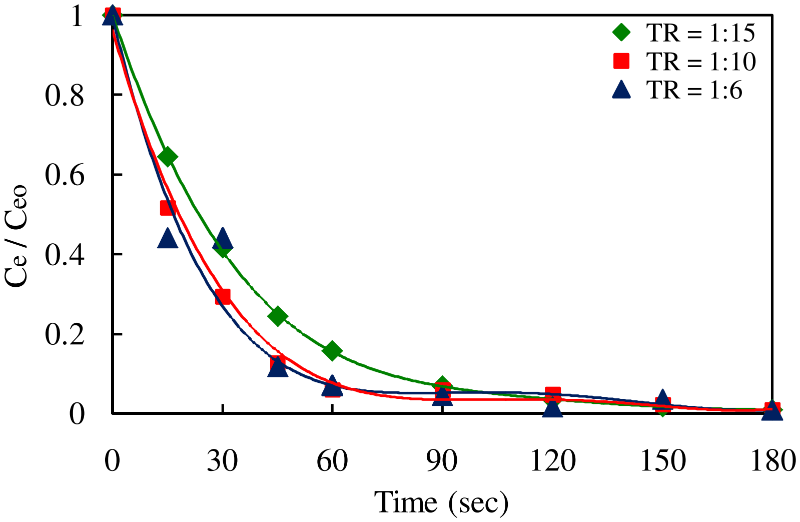


Fig. 4.10: Effect of treat ratio on rate of copper extraction using 10% (v/v) LIX 84I (ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, Cc=10% (v/v), pH=8.1, Ceo≈ 500 mg/L, N=160 rpm).

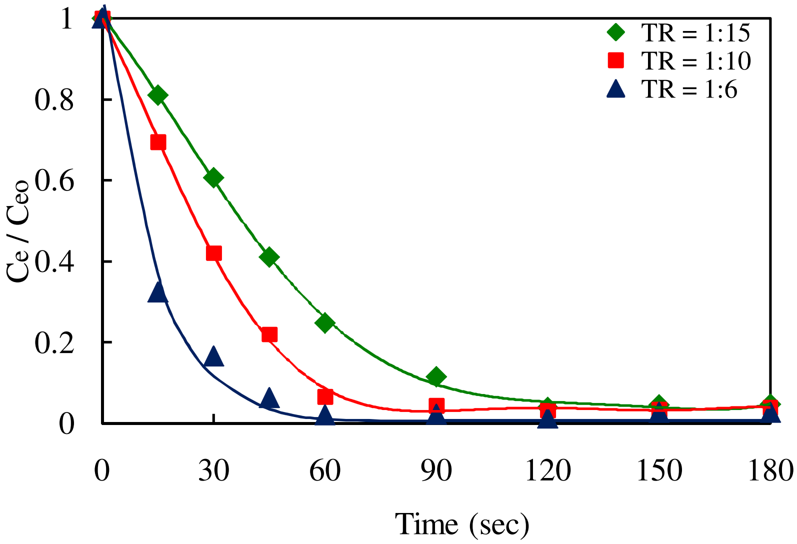


Fig. 4.11: Effect of treat ratio on rate of copper extraction using 5% (v/v) LIX 84I (ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, Cc=5% (v/v), pH=8.1, Ceo≈ 500 mg/L, N=160 rpm).

Fig. 4.10 shows the extraction curves, it is seen that all the curves converge after 2 min contact indicating same overall extent of extraction but in the first 90 s of extraction there is considerable difference in the extraction rates for TR=1:6 and TR=1:15. Similarly there is a difference in extraction curves for TR=1:6 and TR=1:10 but to a lesser extent. The observed difference in extraction rates stem from the reduction in loading capacity of the oil membrane, due to reduction in the amount of carrier and the oil phase. This effect is even more prominently seen in Fig. 4.11.

Fig. 4.11 that presents the extraction curves for variation in treat ratio using emulsions with 5% (v/v) LIX 84I as carrier under otherwise identical conditions. It is seen that the extraction curves obtained for treat ratio 1:6, 1:10 and 1:15 all diverge out although the final extent of extraction in all three cases is almost the same. The overall rates observed for treat ratio variation using emulsions containing 5% (v/v) LIX 84I are influenced not only by the decline in loading but also a corresponding decrease in stripping capacity as well as contact areas at the external and internal interfaces.

4.4 Extraction of zinc from ammoniacal solutions into ELMs

The extraction of zinc by LIX 84I can be represented by the equilibrium

$$[Zn^{2+}]_A + [2HR]_O \leftrightarrow [ZnR_2]_O + [2H^+]_A \qquad \ldots\ldots(4.2)$$

where HR denotes the extractant and subscripts A and O denote the aqueous and organic phases respectively. The above equation indicates that the pH of the aqueous phase should decline as extraction proceeds since two protons are released into the aqueous phase for every mole of zinc extracted in the organic phase. Experimental studies with LIX 34 by Hoh *et al.* (1982), Hostarex DK16 by Rao *et al.* (1992) and LIX 54 by Alguacil and Cobo (1998) showed that percentage Zn extraction from ammoniacal media increases up to pH 7.8 – 8.1 and thereafter declines. The decline with increasing pH can readily be explained by Eq. (4.3) (Kordosky 1979).

$$[Zn(NH_3)_4^{2+}]_A + [2HR]_O \leftrightarrow [ZnR_2]_O + [2NH_3]_A + [2NH_4]_A \qquad \ldots..\ (4.3)$$

The ammonia in the solution functions as a coordinating ligand that competes favorably with the organic extractant for the metal ion. Stoichiometric excess of ammonia in the aqueous phase leads to the formation of a zinc-ammine complex with the metal ion in the aqueous phase, resulting in a decrease in the extent of extraction. In an ELM system, these effects get compounded since at higher pH even free ammonia is transported and trapped within the membrane. Lee and Chan (1990) have shown that free ammonia transport occurs at aqueous phase pH >11. They observed that at pH 9.5 the free ammonia content in the aqueous solution was 50% while at pH 8 it was less than 10%. It appears that ammoniacal solutions at pH~8 are most appropriate for extraction of zinc. Under such conditions the metal ion would be largely free to complex with the extractant and free ammonia concentration would be reasonably low for ammonia to get transported into ELMs and deplete the stripping acid concentration. In view of this, the effect of pH on extent of extraction was first established and discussed in Section 4.4.1.

In an earlier investigation Sengupta *et al.* (2006, 2007) showed that emulsions formulated with Span 80 having concentration of 3%wt (of oil phase) was adequate for membrane stability. Hence, all emulsions were formulated with 3%wt Span 80. The emulsions were dispersed at stirring speed of 160 rpm that resulted in a uniform dispersion of emulsion globules in the feed phase.

The parameters affecting the extraction rates are internal phase volume fraction (ϕ), extractant concentration (Cc) in the membrane phase, internal phase acid concentration (Cio). These three parameters reflect the emulsion properties, other parameters influencing rates are feed phase pH, treat ratio (TR) and initial feed concentration (Ceo). Metal extractions are known to be very sensitive to pH of the media, hence the effect of pH was investigated prior to the study of other parameters.

4.4.1 Effect of pH

The rates of extraction were established at three pH values 7, 8.1 and 8.6 and the results are presented in Fig. 4.12.

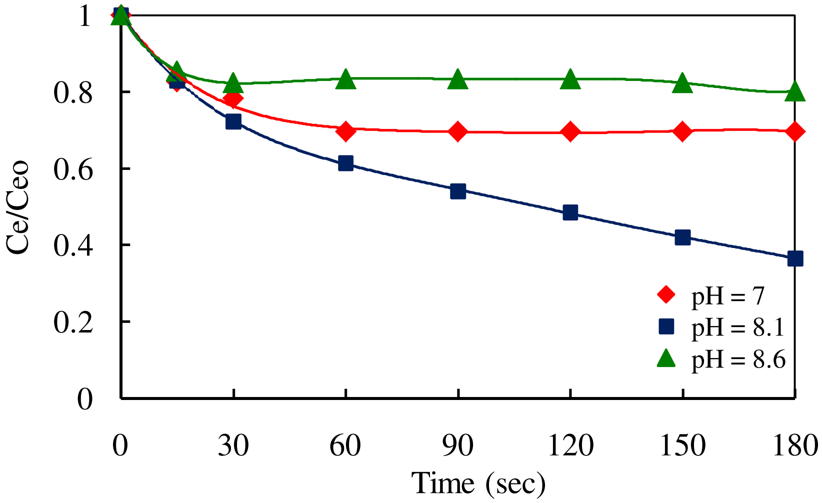


Fig. 4.12: Effect of feed pH on rate of zinc extraction
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, Cc=10% (v/v), Ceo≈ 1000 mg/L, TR=1:6, N=160 rpm).

It was observed that at pH 8.1, the extent of extraction was substantially greater in comparison with the other pH values. At pH 8.6, only 20% of the initial Zn was extracted. This behavior is likely due to the formation of the zinc ammine complex in the ammoniacal solution leaving small amount of free zinc to complex with the extractant and get extracted.

At pH 7 about 30% of Zn was extracted in a minute and thereafter no further extraction took place. This behavior could be attributed to the pH equilibrium of Zn - LIX 84I systems (Cognis Corporation, MCT Redbook 2007).

4.4.2 Effect of carrier concentration (Cc)

The effect of carrier concentration is shown in Fig. 4.13 and as expected, increasing the extractant concentration from 5% (v/v) to 10% (v/v) gives a 20% enhancement in the amount extracted.

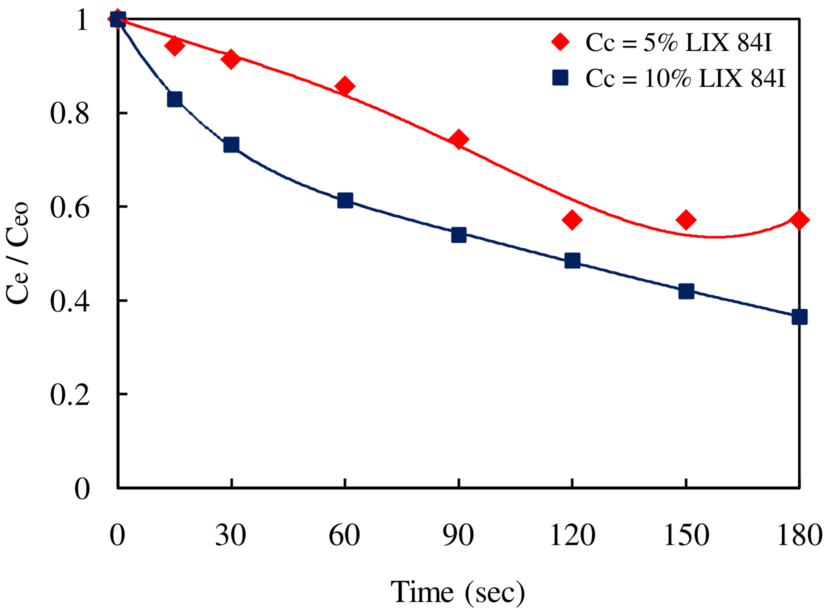


Fig. 4.13: Effect of carrier concentration on rate of zinc extraction (ϕ=0.5, W_{surf}=3 wt%, Cio=1.5 M, pH=8.1, Ceo≈ 1000 mg/L, TR= 1:6, N=160 rpm).

It is noteworthy that under identical conditions in the case of copper extraction from ammoniacal media it was found that LIX 84I concentration in the membrane phase in the range of 2% (v/v) to 10% (v/v) did not influence the rate of extraction of copper as observed by Sengupta *et al.* (2007).

4.4.3 Effect of internal phase acid concentration (Cio)

An increase in the internal phase stripping acid concentration increases the rate and extent of extraction as shown in Fig. 4.14.

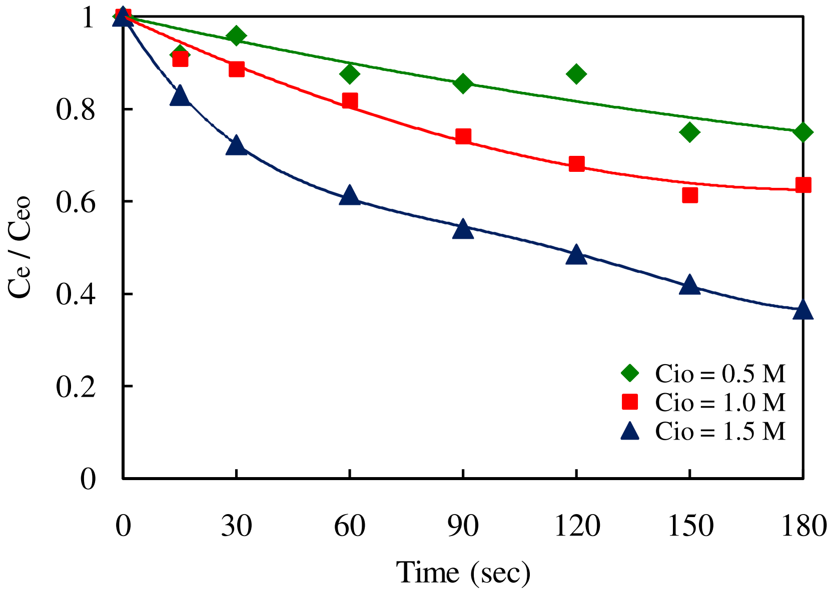


Fig. 4.14: Effect of internal phase acid concentration on rate of zinc extraction (ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cc=10% (v/v), Ceo≈ 1000 mg/L, TR=1:6, N=160 rpm).

When Cio was 0.5 M, the rate of extraction was minimum, while at Cio=1.5 M the rate of extraction was maximum. At Cio=1.0 M the rate was intermediate to the other two conditions, but rates are relatively closer to the case where Cio was 0.5 M.

4.4.4 Effect of internal phase volume fraction (ϕ)

A change in the internal phase volume fraction ϕ changes the emulsion morphology, influences the rates of extraction as well as the stability of the emulsion. All sensible properties of the emulsion change with change in ϕ. Increase in ϕ leads to an increase in the amount of stripping phase in the emulsion, thereby, increasing its extraction capacity. It also leads to a decrease in the diffusional resistance of the metal-oxime due to the formation of thinner membranes. The effect of ϕ is shown in Fig. 4.15.

Contrary to expectation of rapid diffusion and faster extraction with thinner membranes, it is seen that an increase in ϕ from 0.5 to 0.64 leads to a substantial decrease in the amount extracted. The lower rate of extraction stems from a number of physico-chemical changes with increase in ϕ; predominantly among them are the decrease in extractant concentration present in the system for a given emulsion hold-up and the increase in internal drop sizes.

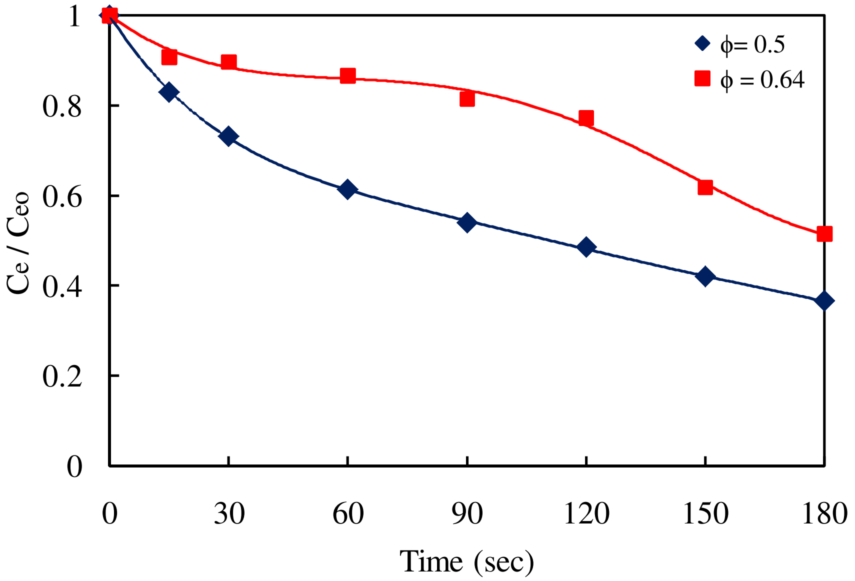


Fig. 4.15: Effect of internal phase volume fraction on rate of zinc extraction (pH=8.1, W_{surf}=3 wt%, Cio=1.5 M, Cc=10% (v/v), Ceo≈ 1000 mg/L, TR=1:6, N=160 rpm).

The Sauter mean diameter d_{32} for emulsions with ϕ=0.5 were found to be 2.72 μm while that for ϕ=0.64 were 10.74 μm. This large increase in d_{32} contributes to a decrease in internal phase stripping areas, which is not adequately compensated by the reduction in membrane thickness.

4.4.5 Effect of initial feed concentration (Ceo)

The effect of initial [Zn] concentration in the feed on the rate of zinc extraction were investigated using emulsions having ϕ=0.5, W_{surf}=3% wt of membrane phase and Cio=1.5 M. The initial pH and treat ratio were maintained at 8.1 and 1:6 respectively.

Extraction results are shown in Fig. 4.16, which is a plot of change in zinc concentration in aqueous phase with time. The pattern of zinc loading in ELMs along with a quantitative assessment of the amount of zinc stripped in the internal stripping phase of the emulsion, after a 180 s contact between the feed and the ELMs, for initial feed concentration variations is shown in Fig. 4.17.

It was observed that as the initial feed concentration increased, the extent of zinc extraction into ELMs also increased. When zinc loading was low most of the zinc extracted in the ELMs got stripped in the internal phase of the ELMs. However, at high zinc loadings the amount of zinc stripped in the internal phase of the ELMs did not increase substantially, hence most of the zinc extracted by the ELMs was retained in the membrane phase.

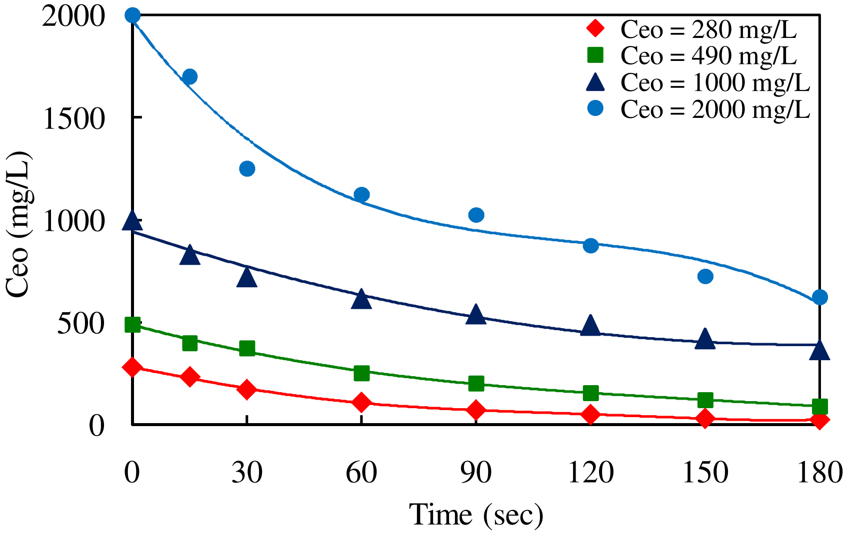


Fig. 4.16: Effect of initial feed concentration on rate of zinc extraction
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.5 M, Cc=10% (v/v), TR=1:6, N=160 rpm).

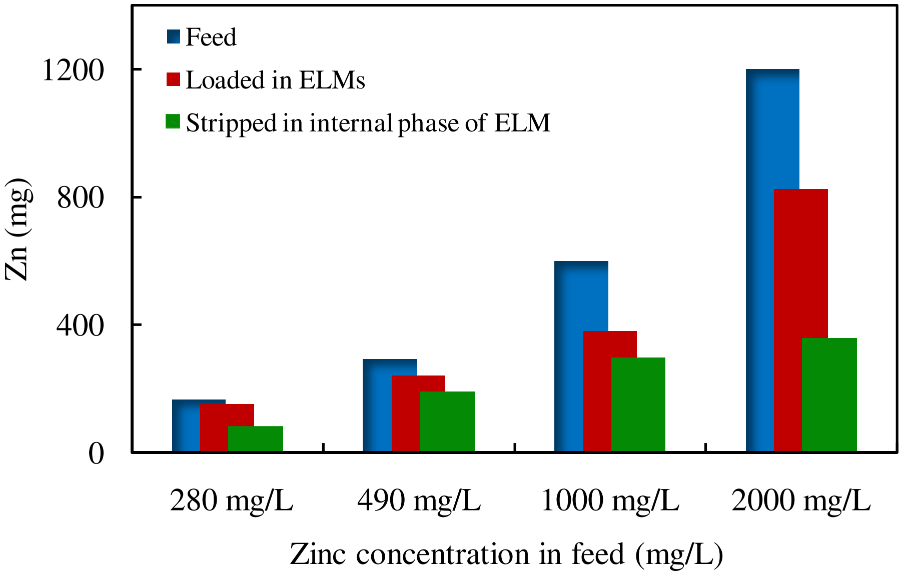


Fig. 4.17: Zinc extraction, stripping patterns in ELMs

The low rate of zinc stripping could be attributed to the slow stripping kinetics as well as the diffusional effects that play an important role in further slowing down the stripping rates. High values of Ceo lead to greater zinc loadings in the ELMs causing quick saturation of the peripheral internal phase droplets in the emulsion necessitating deeper penetration of the Zn–oxime complex within the emulsion globules to get stripped.

When Ceo was 2000 mg/L the net zinc uptake by the emulsion was 825 mg, out of which, zinc retained in the membrane phase of the emulsion was as high as 468 mg. Whereas, when Ceo was 1000 mg/L, the net Zn uptake by the emulsion was 380.5 mg out of which zinc accumulated in the membrane phase was only 85.3 mg. To assess the extent of zinc stripped during the time span of the experimental runs, a number of experiments were carried out with zinc concentration Ceo=1000 mg/L at the (above) specified operating and emulsion conditions. These experiments were stopped at time intervals of 60,120,150 and 180 s. The emulsions were quickly separated from the feed and demulsified. The internal phase was analyzed for zinc.

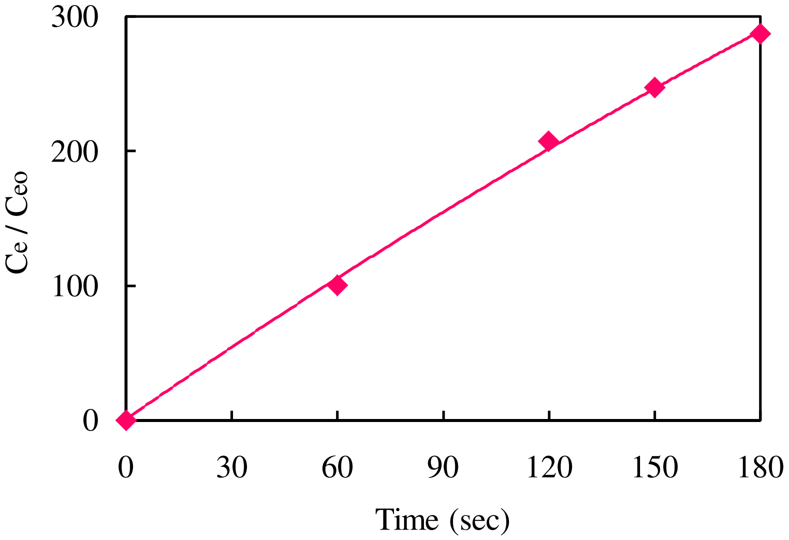


Fig. 4.18: Stripping rate of zinc within ELMs

Although such data is not exact, due to the time delay of 2 - 3 min for emulsion separation from feed, during which the stripping reaction continues, it does provide a representative idea of the amount stripped with time. The results of these experiments show a linear relationship indicating a constant rate of zinc stripping under the experimental conditions as shown in Fig. 4.18.

4.4.6 Effect of treat ratio (TR)

The treat ratio in an ELM extraction is the ratio of emulsion phase to feed phase. It is identical to solvent to feed ratio in conventional liquid extraction. Increasing the treat ratio generally leads to an increase in the loading capacity and the rate of extraction. This is because there is an increase in emulsion volume in the system and correspondingly an increase in the carrier, strippant amount and also overall surface area for mass transfer.

Fig. 4.19 shows the effect of treat ratio on the extraction of zinc from ammoniacal solutions. As the treat ratio increased there was an increase in the extent of extraction as well as the extraction rates, but the increase was sharp when treat ratio increased from 1:15 to 1:10 in comparison to the increase in treat ratio from 1:10 to 1:6. This pattern could be attributed to a possible increase in globule size distribution due to increased hold-up of the emulsion. Sengupta *et al.* (2006) have observed a strong decline in extent and rates of extraction when treat ratios were increased from 1:6 to 1:4 due to increased globule size distribution at larger emulsion hold-ups.

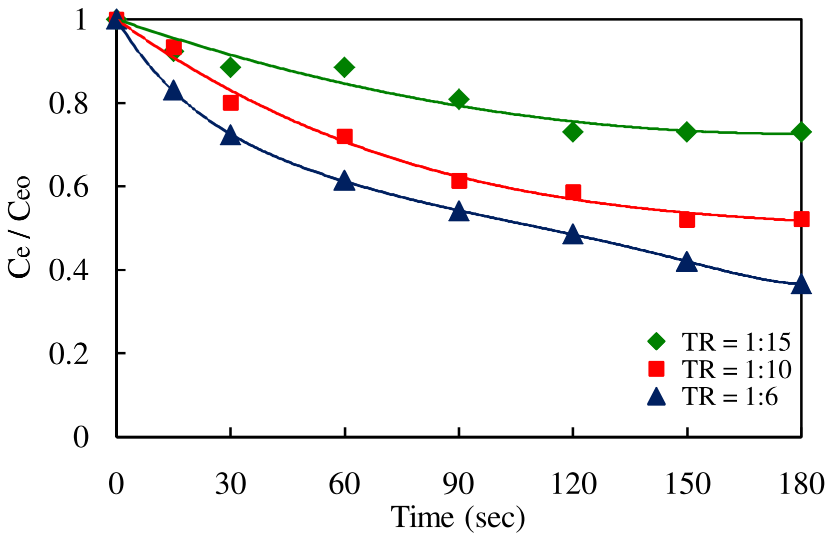


Fig. 4.19: Effect of treat ratio on rate of zinc extraction
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.5 M, Cc=10% (v/v), Ceo≈ 1000 mg/L, N=160 rpm).

Formation of larger sized globules not only reduces the external surface areas but also increases the effective diffusive path lengths within the globule that results in a decline in the extraction rates. In the present investigation treat ratios of 1:15, 1:10 and 1:6 were used resulting in stripping acid to zinc molar ratios of 3.27, 4.9 and 8.18 respectively. These values indicate a substantial increase in extraction capacity when treat ratio was increased from 1:10 to 1:6 but at the same time, due to the increase in emulsion hold-up, the globule size distribution also tended to shift towards larger sizes resulting in a decrease in rates. The combined effect culminates in the behavior observed in Fig. 4.19.

4.5 Zinc extraction and stripping from ammoniacal solutions

ELMs are complex systems with extraction and stripping phenomena encountered simultaneously at the external feed - membrane interface and the membrane - strippant interface within the emulsion globules. Both these phenomena are equilibrium limited and proceed at finite rates. Further the physico - chemical features of the emulsion influence the transport rate of the metal from the feed - membrane interface to the membrane - strippant interface. If the equilibrium conditions are adequately taken care of them any one of the three kinetic steps could be the rate controlling one. If the loading kinetics is rate controlling then it is expected that the metal retention in the membrane phase would be negligible. However, if the stripping was the rate-limiting step then metal retention in the membrane phase would build up with time along with a decline in the loading rates since the extractant would not be free to bind the metal. Qualitatively, almost a similar situation would exist if diffusion was the rate-limiting step. It is difficult to discern the exact mechanism in ELM extractions because of the short contact times and the change in pH at the feed–membrane interface with progress of the extraction, as well as the inter-connectedness of the various mechanisms.

Hence, to get a quantitative assessment of the individual steps involved in the ELM processes, experiments were carried out to independently study the loading and stripping of zinc using LIX 84I by contacting equal volumes (50 ml) of kerosene containing 10% (v/v) of the extractant with aqueous ammoniacal solution containing 1000 mg/L Zn at an initial pH 8.1. The pH change and amount of zinc loaded in the oil phase were recorded with time for a period of 180 s corresponding to time of contact in an ELM system. Subsequently, zinc was stripped by contacting equal volumes of loaded oil phase with an aqueous strip solution containing 1.5 M H_2SO_4. The amount stripped at definite time intervals was recorded. Loading and stripping results with time are shown in Fig. 4.20 Initial rates of loading were steeper than the rates of stripping indicating that the stripping kinetics were slower than the loading kinetics.

The stripping rates have a considerable influence on the overall rates of extraction in ELM systems, particularly at high feed concentrations leading to large membrane loadings. Even in the case of copper extraction from ammoniacal solutions, it was observed that while loading was instantaneous, stripping was relatively slow and was also influenced by the carrier concentration. The decline in extraction rates at high copper loadings in ELM systems were attributed to the slow stripping rates (Sengupta *et al.* 2007).

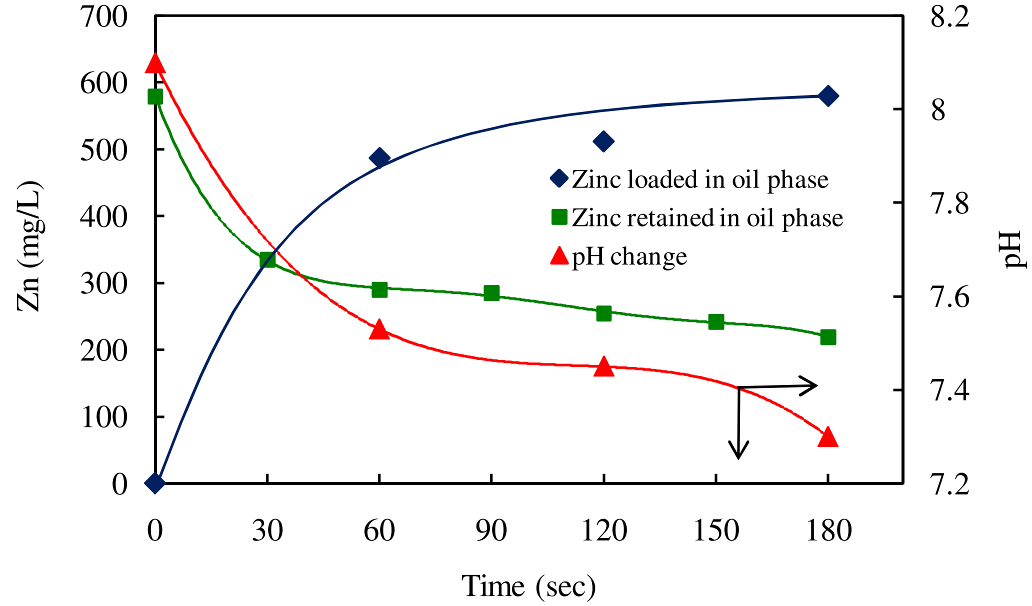


Fig. 4.20: Loading and stripping patterns of zinc
(Cio=1.5 M, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, TR=1:1)

4.6 Co-extraction and stripping of copper and zinc from ammoniacal solutions

Prior to simultaneous extraction of copper and zinc in ELM systems, the nature of simultaneous stripping of copper and zinc from the oil phase was investigated by loading the metals from a mixture of their aqueous ammoniacal solutions at an initial pH of 8.1. The loaded oil phases were then stripped with 1.5 M H_2SO_4 by contacting equal volumes of the metal loaded oil and the stripping phases for a time span of 180 s. Table 4.1 lists the initial conditions of metal concentration for simultaneous loading of the metals in the oil phase, amount of metal stripped from oil phase and separation factor defined as:

$$\beta_{Cu/Zn} = \frac{\left(Cu/Zn\right)_{oil}}{\left(Cu/Zn\right)_{feed}}$$

It was found that zinc loading in the oil phase substantially increased in the presence of copper as seen in Table 4.1, indicating a synergistic influence. Furthermore, it was observed that zinc gets stripped more rapidly in comparison with copper when the zinc concentration was comparable to or more than the copper concentration as seen in Fig. 4.21 (a) and (c).

Table 4.1: Simultaneous loading and stripping patterns of Cu–Zn from ammoniacal solutions

	Initial feed concentration (mg/L)		Amount loaded in oil phase (mg/L)		Amount stripped from loaded oil phase (mg/L)		Separation factor (β)
	Cu	Zn	Cu	Zn	Cu	Zn	
a	1705	230	1705	166	1411.9	50	1.4
b	257	1500	257	1374	140.7	1037.1	1.1
c	1000	820	1000	740	671	689.9	1.1

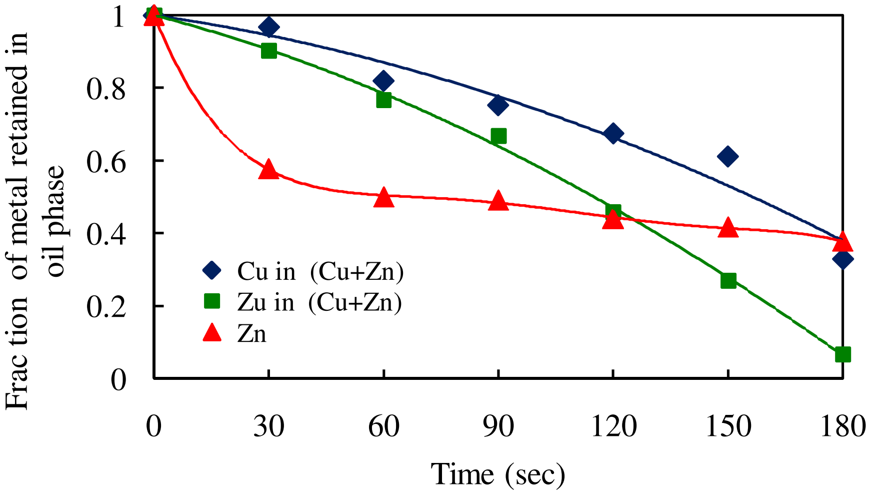


Fig. 4.21 (a): Stripping patterns of Cu-Zn mixture: copper Ceo=1705 mg/L, zinc Ceo=230 mg/L

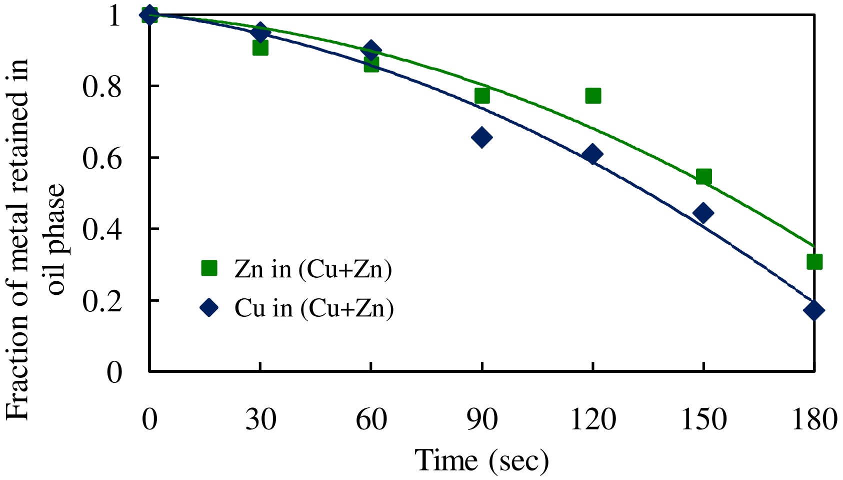


Fig. 4.21 (b): Stripping patterns of Cu-Zn mixture: copper Ceo=257 mg/L, zinc Ceo=1500 mg/L

Even the extent of zinc stripping is more in the presence of copper. However, the initial rate of zinc stripping in absence of copper was very rapid but quickly settled to a constant value and the overall extent of stripping was also lower as seen in Fig. 4.21. When the copper concentration was greater than zinc in the oil phase, copper stripped faster than zinc as seen in Fig. 4.21 (b). The plateau region observed during stripping in Fig. 4.21 (c) is inexplicable, but could be due to competitive mechanism of stripping–loading–stripping in acidic media. However, conclusive analysis is currently beyond the scope of this work and calls for more detailed investigation.

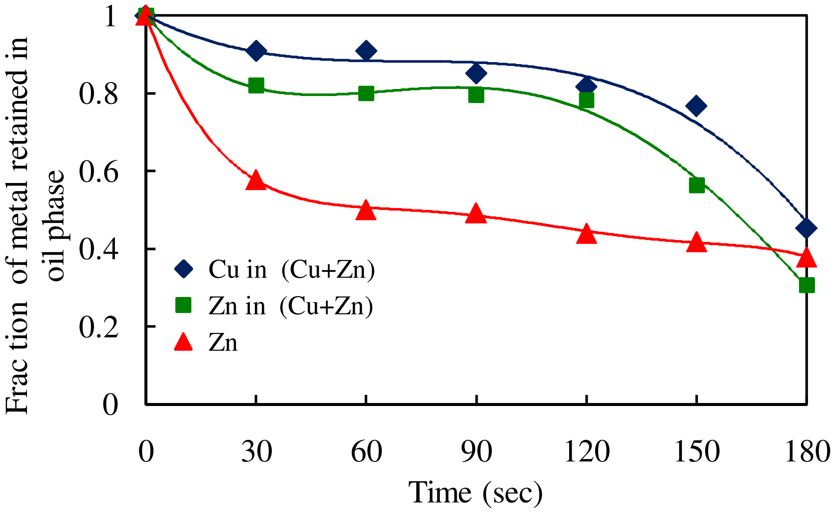


Fig. 4.21 (c): Stripping patterns of Cu-Zn mixture: copper Ceo=1000 mg/L, zinc Ceo=820 mg/L

The IR spectra of the LIX 84I complex with copper, zinc and simultaneously with copper–zinc mixtures are shown in Fig. 4.22. The band in the region 3500 - 3200 cm^{-1} appears in the spectra of all the complexes and is representative of the characteristic stretching vibration of the intermolecular hydrogen bond in the oxime (Yang *et al.* 2006). All spectra have strong peaks around 3200 - 2800 cm^{-1} that are characteristic peaks of chelated OH groups (Nakamoto 1963). The small peaks around 1025 cm^{-1} could be attributed to the presence of ammonia in the extracted solutions (Alguacil *et al.* 2001).

Note should be taken of the small peak around 800 - 700 cm^{-1} appearing in the spectra. These bands are attributed to the oxime - metal complexes (Yang *et al.* 2006). Classically for coordination compounds, peaks appearing in the region 850 - 650 cm^{-1} are attributed to rocking frequencies. After extensive studies on ammine complexes, Svatos *et al.* (1957) found rocking frequency was most sensitive to the central metal ion. Fig. 4.22 shows the augmentation of the peak observed at 757 cm^{-1} with the metal in the order Cu - Zn > Zn > Cu which also corresponds to the ease of stripping observed in this investigation.

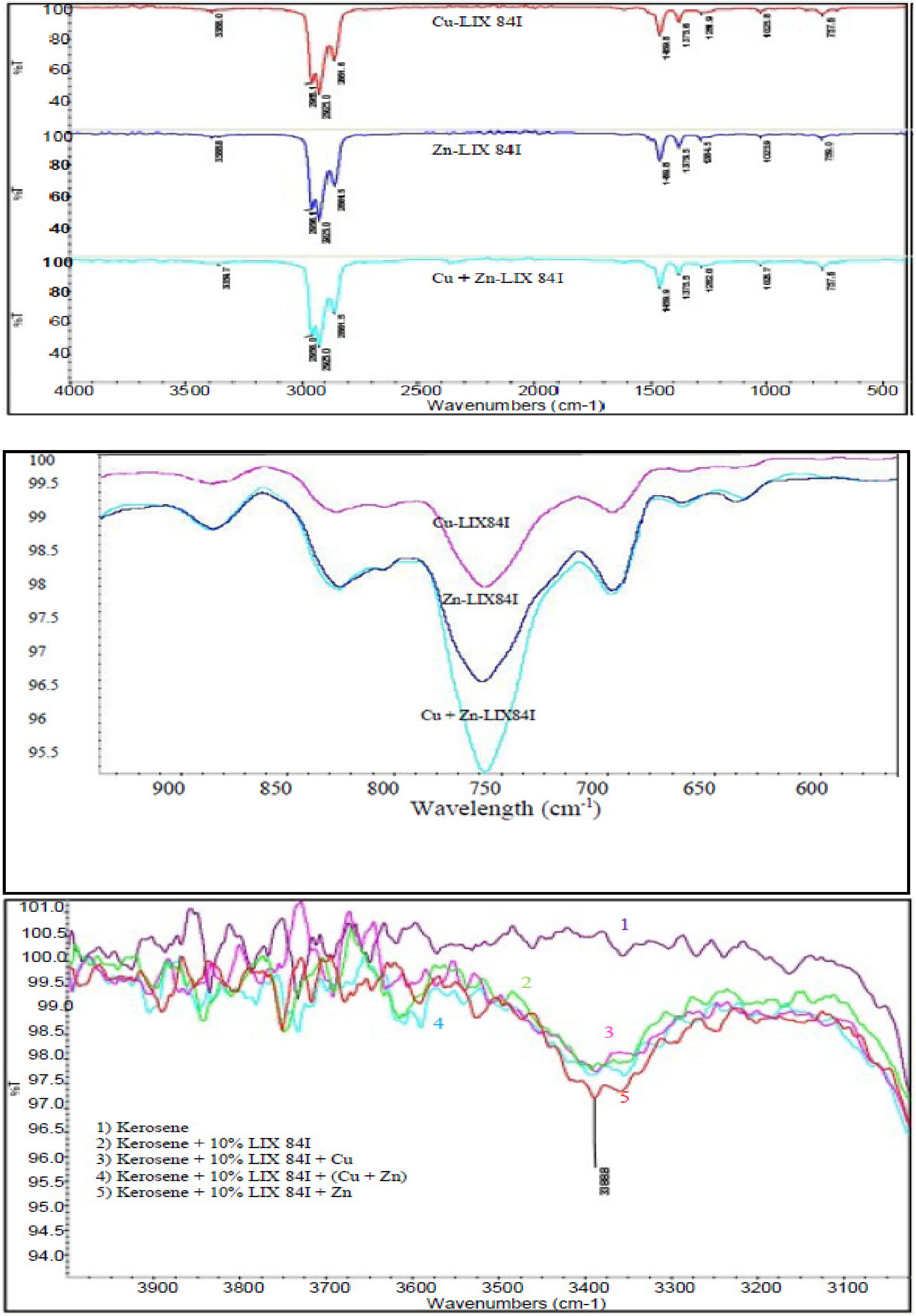


Fig. 4.22: IR spectra of LIX 84I metal complexes

4.7 Co-extraction of copper and zinc into ELMs

Simultaneous extraction of zinc and copper from ammoniacal solutions was investigated using ELMs having ϕ=0.5, Cc=10% (v/v) LIX 84I in membrane phase, W_{surf} =3 wt% membrane phase with treat ratio 1:6. The desired feed solutions were prepared by dissolving requisite amounts of copper sulphate, zinc sulphate and ammonium sulphate (50 g/L) in deionised water and the pH was adjusted to 8.1 using ammonium hydroxide. The effects of the strip acid concentration and the initial concentrations of zinc and copper in the feed on the rates of extraction were investigated.

4.7.1 Effect of internal phase acid concentration (Cio)

Internal phase acid concentrations were varied from 0.5 M to 1.5 M. The initial feed concentrations of zinc and copper, though not exactly same, were comparable. The zinc concentration ranged from 880 to 1037 mg/L and the copper concentration ranged from 990 to 1032 mg/L. Extraction results are shown in Fig. 4.23.

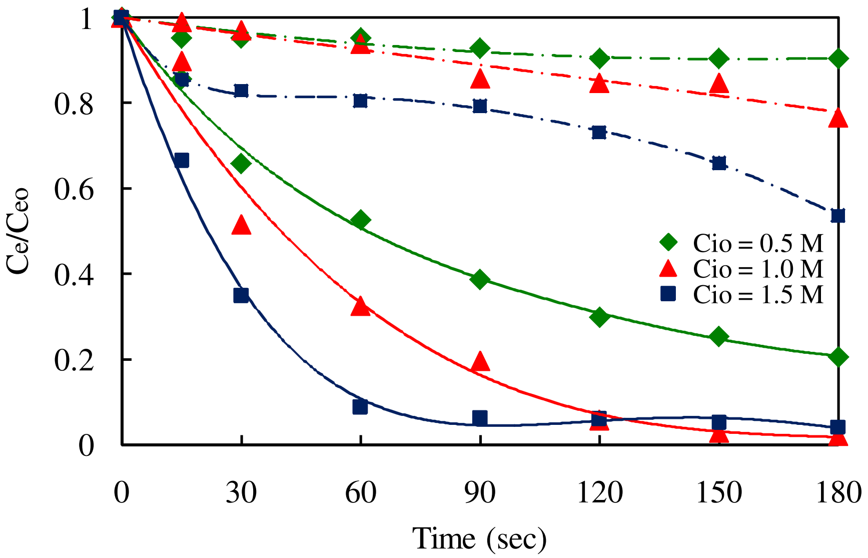


Fig. 4.23: Co-extraction of Cu–Zn into ELMs: effect of Cio (—— Cu, ----- Zn).
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cc=10% (v/v), TR=1:6, N=160 rpm).

It is clear that the rate of extraction of both zinc and copper increased with stripping acid concentration. However, the rates of copper extraction were much larger than that observed for zinc. Moreover, while copper was almost quantitatively extracted in 180 s into ELMs having Cio of 1.0 M and 1.5 M, even in the best case only 50% Zn was extracted in the same time with emulsions having Cio=1.5 M. Comparing Fig. 4.14 with Fig. 4.23 the effect of Cio on zinc extraction in the presence of copper is identified. There was a significant decline in the extent and rates of zinc extraction in the presence of copper. This behavior is contrary to the loading and stripping behavior of copper and zinc shown in Table 4.1 and Fig. 4.21(a). During the simultaneous loading and stripping of copper and zinc it was observed that zinc loads to a greater extent in the presence of copper and also strips faster and to a greater extent in the presence of copper. This pattern should also be true with ELMs.

However, it is noteworthy that in ELMs, loading and stripping occur simultaneously and the large difference in rates observed in Fig. 4.22 could only be attributed to the loading behavior of the metal and the affinity of the oxime for copper. The higher loading capacity and loading rate of the oxime for copper masks the slow stripping kinetics as well as the diffusional effects caused by the various physico-chemical factors.

4.7.2 Effect of initial feed concentration (Ceo)

Three variations of the initial feed concentrations were explored ranging from feeds where copper concentration was in large excess in comparison with zinc, when copper and zinc concentrations were comparable and when zinc concentration was much larger than copper. Furthermore, the total metal concentrations in the feeds were also comparable ranging from 1757 mg/L to 1935 mg/L. The ELMs used had Cio=1.5 M all other conditions remained identical.

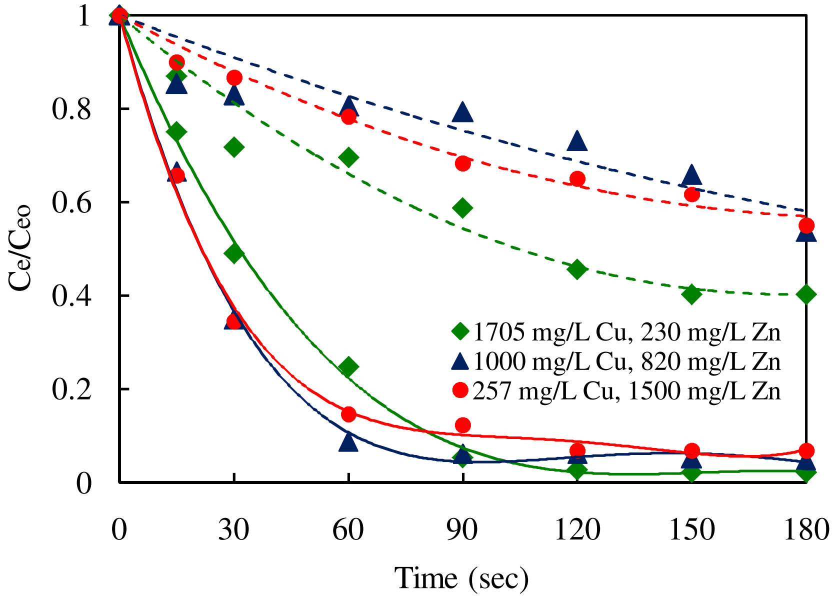


Fig. 4.24: Co-extraction of Cu–Zn into ELMs: effect of Ceo (——Cu, ----- Zn).
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.5 M, Cc=10% (v/v), TR=1:6, N=160 rpm).

Extraction results are shown in Fig. 4.24. In all three cases copper extraction was much faster than zinc and almost quantitative removal of copper took place within 180 s while a maximum of 55% Zn removal took place in the same time duration and that too when its concentration in feed was quite low.

Table 4.2 details the quantitative aspects of the Cu–Zn separation using ELMs. It is distinctly observed that ELMs with LIX 84I show a preference for the selective removal of copper from Cu–Zn mixtures. All other considerations including stripping kinetics of copper and zinc along with other physicochemical features such as diffusion of the oxime complex within the emulsion globule etc are completely masked by the affinity of the oxime for copper. The separation factor $\beta_{(Cu/Zn)}$ obtained at time duration of 120 s, corresponding to onset of maximum copper removal, ranged from 1.8 to 3.5 is shown in Table 4.2.

Table 4.2: Extraction and stripping of Cu–Zn in ELMs

	Initial feed conc. (mg/L)		Net amount in feed (mg)		Amount loaded in ELM (mg)		Amount stripped in internal phase of ELM (mg)		Separation factor (β)
	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	
a	1705	230	1023	138	1000.6	82.5	626.5	82.5	3.5
b	257	1500	154.2	900	143.6	405	138	345	1.8
c	1000	820	600	492	571.3	228	197.1	146	2.7

It was found that ELMs loaded with LIX 84I had the efficacy of removing zinc as well as mixtures of copper and zinc from aqueous ammoniacal media. Furthermore, they can also be used for selective removal of copper from Cu–Zn mixtures in ammoniacal media. Copper from zinc with separation factor $\beta_{(Cu/Zn)}$=3.5. These ELMs could be used for treating the ammoniacal wastewaters obtained from PCB manufacturing units containing Cu–Zn mixtures.

4.8 Extraction of nickel from ammoniacal solutions

Increasing interest in metal recovery from Indian Ocean manganese nodules led to the development of hydrometallurgical processes for simultaneous separation of nickel, copper, manganese and other metals from ammoniacal leach solutions. Ammoniacal leaching is otherwise also an attractive approach to process laterite ores, electronic wastes, sludge, spent catalysts and other raw materials and concentrates containing nickel, copper, zinc, cobalt and other heavy metals.. There are two basic process alternatives for metal separation in a multi-component system using solvent extraction: selective extraction and selective stripping. In most cases selective stripping is more economical because it requires fewer stages than for selective extraction.

Merigold and Jensen (1974) were the first to describe the coextraction of copper and nickel from an ammoniacal laterite leach solution, but they did not use selective stripping technique for metal recovery from organic phase. The separation of copper and nickel from ammoniacal solutions also containing cobalt in conjunction with the processing of manganese nodules has been extensively studied by the Ledgemont laboratory (Agarwal 1979).

Early investigations by Siemens and Corrick (1977) described the co-extraction-selective stripping process as applied to nickel laterite leach liquors. Nickel and copper were extracted in three stages using a 12% (v/v) solution of LIX 64N in kerosene. Nickel stripping was carried out in five stages with spent nickel electrolyte having ~ 5 kg / m^3 H_2SO_4 and copper was stripped with spent electrolyte containing ~ 175 kg / m^3 H_2SO_4. Rhoads *et al.* (1977) also applied the coextraction selective stripping process to treat leach liquors obtained from nickel laterites using LIX 64N. Agarwal *et al.* (1980) described the stripping of nickel from a copper-nickel loaded LIX 64N. The nickel content in the stripped organic phase was 0.04 kg / m^3. By using a more concentrated sulfuric acid the copper was stripped in two stages. The stripped organic phase retained 0.6 kg / m^3 of copper.

Nilsen *et al.* (1982) reported co-extraction of nickel and copper from ammoniacal-ammonium sulphate leach liquors (pH ~ 9.5) obtained by reduction-roasting of laterites, using LIX 64N at 40°C. Ni and Cu were co-extracted in three stages to an extent > 99%. Selective nickel stripping was carried out to the extent of 99.9%, in 5 stages followed by copper stripping in one stage. Bhaskara Sarma *et al.* (1987) described the co-extraction and selective stripping of copper and nickel from ammoniacal-ammonium sulphate leach liquors obtained from Indian Ocean manganese nodules. The two metals (1.72 kg / m^3 each) were co-extracted using 40% (v/v) LIX 64N as the extractant in two stages.

Sandibigraha and Bhaskara Sarma (1997) used LIX 87QN, a ketoxime based extractant developed for Ni extraction from ammoniacal solutions, to extract both Cu and Ni from ammoniacal solutions. They observed that Ni extraction is extremely sensitive to equilibrium pH. The extraction falls sharply at pH values > 9. Selective nickel stripping was achieved in five stages using nickel spent electrolyte at pH 1.5. Parija *et al.* (1998) extracted nickel from fairly concentrated solutions containing almost 20.5 kg / m^3 Ni using LIX 84I their results indicate that equilibrium pH > 7 is suitable for complete extraction of Ni in < 3 stages.

Parija and Bhaskara Sarma (2000) optimized process parameters for the separation of nickel and copper from an ammoniacal leach liquor obtained by leaching a Cu-Ni-Fe sulfide concentrate using a 40% (v/v) LIX 84 in kerosene solution with an aqueous / oil ratio of 1:2 in two stages. Ni stripping was achieved in four countercurrent stages using spent electrolyte having initial pH of 1.7 with an efficiency of 99.6%.

Recently Hu *et al.* (2012) investigated the extraction behavior of Ni from ammonium sulphate solution using sterically hindered β diketone. They have reported that the extraction efficiency for Ni increases with pH and reaches a maximum at pH 8.5. They further reported that Ni extraction is endothermic at pH 7.5 and exothermic at pH 8.5 and 9.5. Their investigation also revealed that ammonia molecule gets co extracted by coordinating with nickel extracts.

Although nickel extraction from ammoniacal solutions has been investigated over the last 35 years and there are a number of publications that bear testimony to the importance of ammoniacal media as well as the solvent extraction technique but process intensification investigations of recovering nickel alone or from its mixtures with other metal ions using the emulsion liquid membrane technique has not yet been explored. Ni extraction from sulphate media in ELMs has been explored, but it suffers from the drawback of slow stripping kinetics that has inhibited its growth. Therefore there exists considerable interest and potential to extract Ni from ammoniacal solutions using emulsion liquid membranes.

4.9 ELM extraction of Ni and co-extraction of Ni and Cu from ammoniacal solutions

Investigations on the extraction of Ni from ammoniacal – ammonium sulphate solutions was conducted using water in oil emulsions formulated from kerosene containing LIX 84I as carrier and Span 80 as the emulsifier. The concentration of Span 80 was 3 wt%. Sulfuric acid was used as the aqueous stripping phase of the emulsion. The emulsion was dispersed in the Ni bearing feed stream at an rpm of 160 the treat ratio was maintained 1:6. Initially the effect of pH on the extraction was investigated thereafter at the chosen pH value effects of other process and emulsion parameters were investigated as reported in the subsequent subsections.

4.9.1 Effect of pH

Parija *et al.* (1998) studied the effect of feed solution pH on liquid extraction of nickel from ammonium–ammonium sulphate solution using 40% LIX 84 extractant in kerosene. Their results indicate that nickel extraction increases with increasing equilibrium pH up to pH 8. The extraction isotherm is plotted in Fig. 4.25. Taking clue from these results, investigations were carried out to study the effect of pH on the extraction of nickel in ELMs at pH values of 7 and 8.1 using feed solutions containing fixed ammonium sulphate concentrations of 50 gm/L.

The emulsions were formulated with equal volume of kerosene and stripping phases so that the internal phase volume fraction ϕ=0.5, carrier concentration Cc=10% (v/v) LIX 84I, and the internal phase sulfuric acid concentration Cio=1.0 M. The initial Ni concentration in feed was Ceo=1000 mg/L.

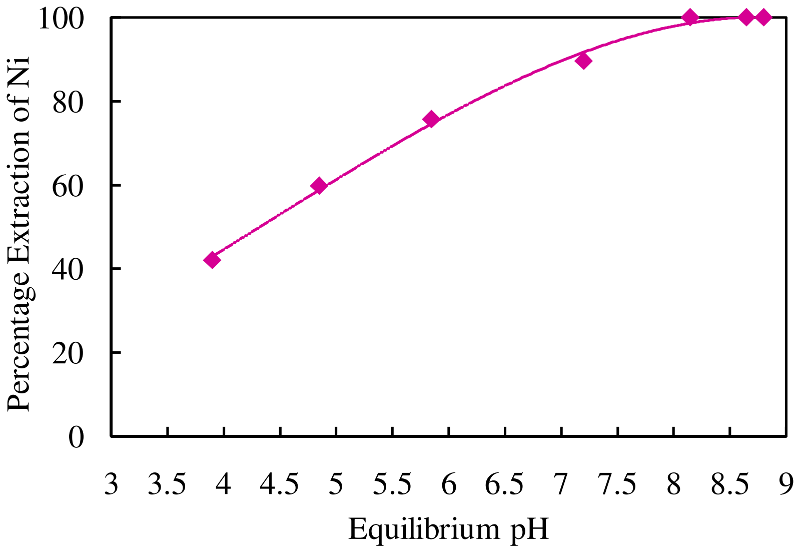


Fig. 4.25: Effect of feed pH on extraction of nickel (Parija *et al.* 1998)

Fig. 4.26 shows that the rate of extraction of nickel in ELMs from ammoniacal-ammonium sulphate solutions is initially rapid and more than 50% of the nickel in feed streams gets extracted in just three minutes at both the pH values. The rate of extraction at pH 8.1 was faster than at pH 7 although the extent of extraction was nearly the same.

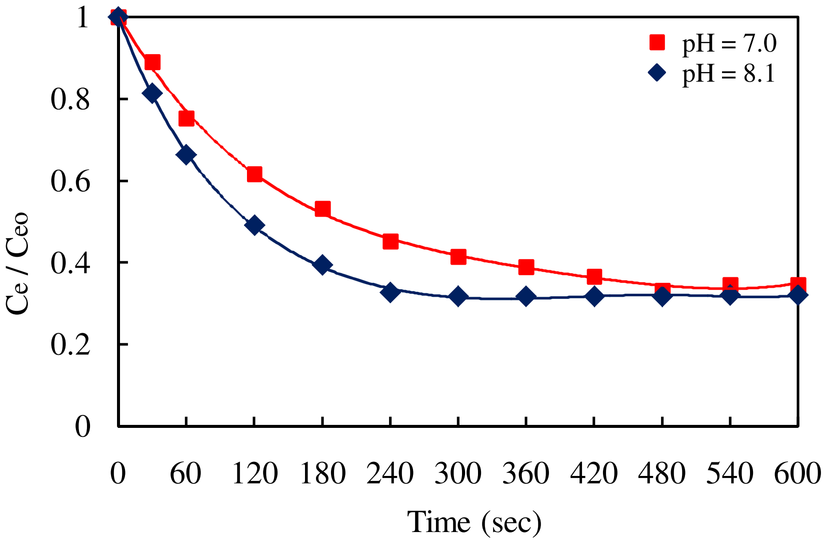


Fig. 4.26: Effect of feed pH on rate of nickel extraction
(ϕ=0.5, W_{surf} =3 wt%, Cio=1.0 M, Cc=10% (v/v), Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

Apparently it appears that the emulsion phase got saturated in 6 – 8 minutes of contact for both the pH values however, that is unlikely to be the only reason because the amount of nickel loaded in the emulsion for the case of pH 8.1 was only 4.08 gm/L of emulsion while the maximum loading capacity reported in the literature by Alguacil and Cobo (1998) for hydroxy oxime based extractant (2-hydroxy -5 nonyl benzaldehyde oxime) is found to be 5.2 gm/L for 10% (v/v) extractant in solvent. This would translate to almost 2.6 g/L for W/O emulsions having ϕ = 0.5 assuming stripping of nickel does not occur. In case nickel stripping takes place simultaneously emulsion loading capacities are likely to be much larger. It was felt that lesser removal of Ni from solutions (68%) could also be attributed to inadvertent pH change. For all further investigations the feed phase pH was fixed at pH 8.1.

After completion of the experimental run, on disintegration of the emulsion to its constituent phases, the aqueous phase of the emulsion was analyzed for the metal content. This gave an idea of the amount of loaded metal stripped in the internal phase of the emulsion. Fig. 4.27 gives a relative assessment of the amount of metal distributed in the aqueous phase under different pH conditions. Amount of metal in the oil phase can be estimated by material balance.

It is observed from Fig. 4.27 that the amount of nickel loaded in the ELMs is nearly the same in both cases and corroborates with Fig. 4.26, however the amount of nickel stripped in the aqueous phase is more at pH of 8.1 in comparison with pH 7.0 which again corresponds to the sharper decline of the extraction profile observed for pH 8.1 in Fig. 4.26.

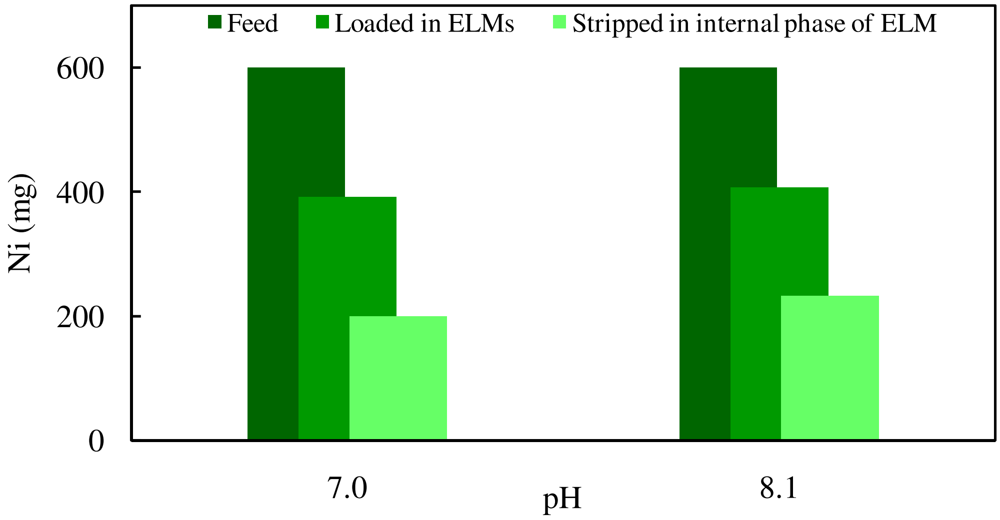


Fig. 4.27: Effect of feed pH on stripping of nickel
(ϕ=0.5, W_{surf} =3 wt%, Cio=1.0 M, Cc=10% (v/v), Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

4.9.2 Effect of internal phase acid concentration (Cio)

The internal phase acid concentration was varied to study the influence of stripping on overall extraction rates. Parija and Bhaskara Sarma (2000) studied separation of nickel and copper from ammoniacal solutions using LIX 84 as extractant and have suggested that reasonable nickel stripping from ammoniacal solutions to the tune of 65% per stage can be obtained by using stripping phase pH 1.75. They also indicated that extent of stripping declined with an increase in pH of the stripping media. In view of these results the pH of the stripping media was modulated to attain quick stripping of the loaded nickel from the membrane phase. Since sulfuric acid was used as the striping agent, the pH of the solution was correlated with the acid concentration and it was found that acid solutions having concentrations 0.05 M, 0.5 M, 1.0 M and 1.5 M resulted in pH 1.72, 1.06, 0.89, 0.79 respectively.

The influence of concentration of H_2SO_4 in the internal phase of the emulsion on the rates of extraction was evaluated at acid concentrations ranging from 0.5 M to 1.5 M. The emulsions used had carrier concentration of 10% (v/v) LIX 84I and ϕ=0.5 with initial nickel concentration Ceo=1000 mg/L.

Fig. 4.28 shows the extraction rates using H_2SO_4 concentration of 0.5 M, 1.0 M and 1.5 M in the stripping phase. It is seen that using 0.5 M acid for stripping in the ELMs resulted in almost 40% removal of nickel in four minutes but thereafter there is an increase in the nickel concentration in the bulk phase indicating breakage of the emulsion after this point of time. With 1.0 M acid in the stripping phase almost 68% extraction took place in about four minutes and breakage behavior was not observed even with prolonged stirring of the solution indicating the formulation generated stable emulsions. When 1.5 M acid was used as the stripping phase of the emulsions the results were worst only 22% extraction was recorded in 10 minutes of contact.

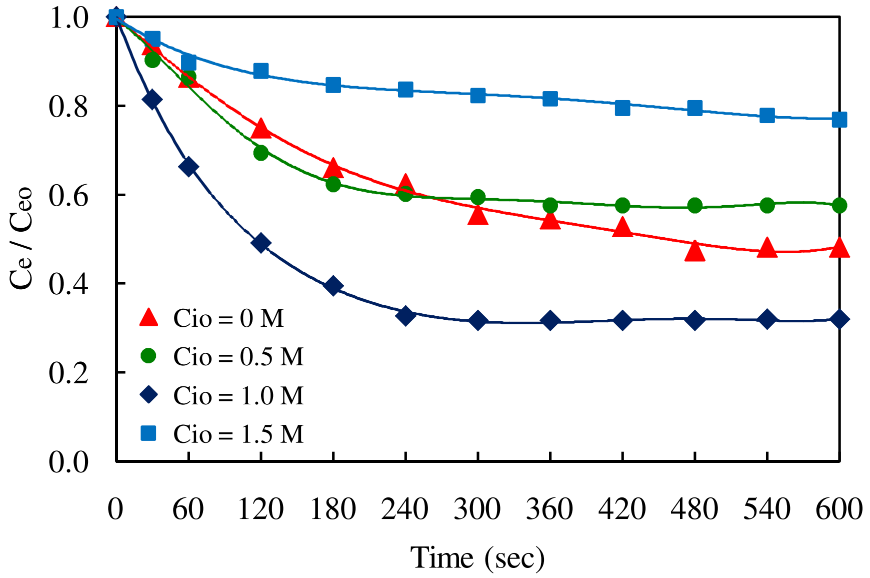


Fig. 4.28: Effect of internal phase acid concentration on rate of nickel extraction (ϕ=0.5, W_{surf}=3 wt%, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

This behavior is attributed to a pH swing that is likely to have taken place during initial dispersion of the emulsion in the feed phase. Such change in pH values could result from minor breakage of emulsion that always takes place during dispersion of the emulsion and could also be due to the adherent aqueous phase on the emulsions. Since the emulsion was formulated with 1.5 M acid even a minor degree of breakage or small amount of adherent aqueous phase could result in reasonable sifting of pH below the value of 8.1 giving rise to conditions not conducive to transfer of nickel in the ELMs.

The understanding of the extraction behavior observed with variation of stripping acid concentration however did not unfold quickly and in this process experiments were repeatedly performed to check the efficacy and repeatability of the data. It is well known that stripping of nickel is slow as reported by numerous investigators, therefore in an initiative to assess whether stripping was at all taking place in the time frame of our experiments; a blank run was also performed by maintaining zero acid concentration in the inner aqueous phase of the ELMs while keeping all other conditions unchanged. These results are also plotted in Fig. 4.28 and it is seen that in this case also almost 50% of the feed nickel was extracted. This extraction is attributed only to the loading of the nickel in the emulsion since the question of stripping did not arise. In this case too minor breakage of emulsion was observed near the end of the run i.e. after 8 – 9 minutes of contact. The overall extraction rates with the blank turned out superior to the extraction patterns observed for both 1.5 M and 0.5 M acid strengths and in a way confirmed that the poor extraction profiles observed with 1.5 M stripping acid was due to pH imbalance rather than anything else.

The final nickel distribution in the stripping phase of the ELM is shown in Fig. 4.29, it is clearly observed that the extent of loading of nickel as well its stripping in the internal phase is the worst for Cio=1.5 M this is primarily attributed to pH decline in the feed during emulsion dispersion in it causing low uptake of nickel. However, even in this case almost 48% of the total nickel loaded in ELMs had got stripped which is nearly the average extent of stripping observed during nickel extraction from ammoniacal media.

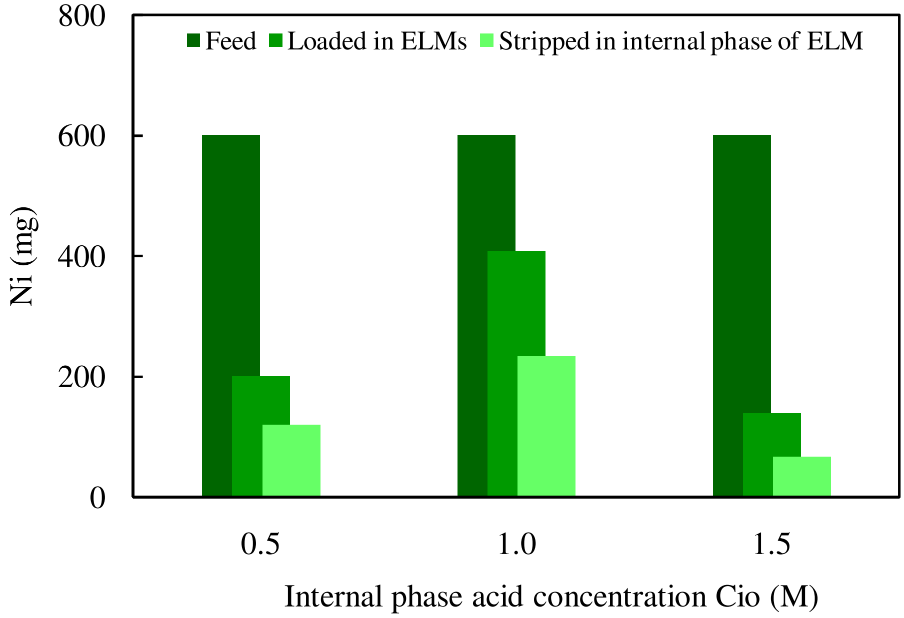


Fig. 4.29: Effect of internal phase acid concentration on stripping of nickel (ϕ=0.5, W_{surf}=3 wt%, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

For the case of Cio=0.5 M again the loading was poor although the extent of stripping of loaded nickel was largest in this case accounting for almost 60% of the total Ni loaded. The extraction profile shown in Fig 4.28 indicates instability in the behavior of the ELMs having Cio=0.5 leading to drop breakage during the time of contact that gets reflected in the overall extraction behavior.

4.9.3 Effect of internal phase volume fraction (ϕ)

A change in the internal phase volume fraction ϕ changes the emulsion morphology and in turn influences the rates of extraction as well as the stability of the emulsion. All sensible properties of the emulsions changes with change in ϕ, in the present study experiments were carried out at ϕ=0.5 and ϕ=0.64 while maintaining all other parameters at a constant value.

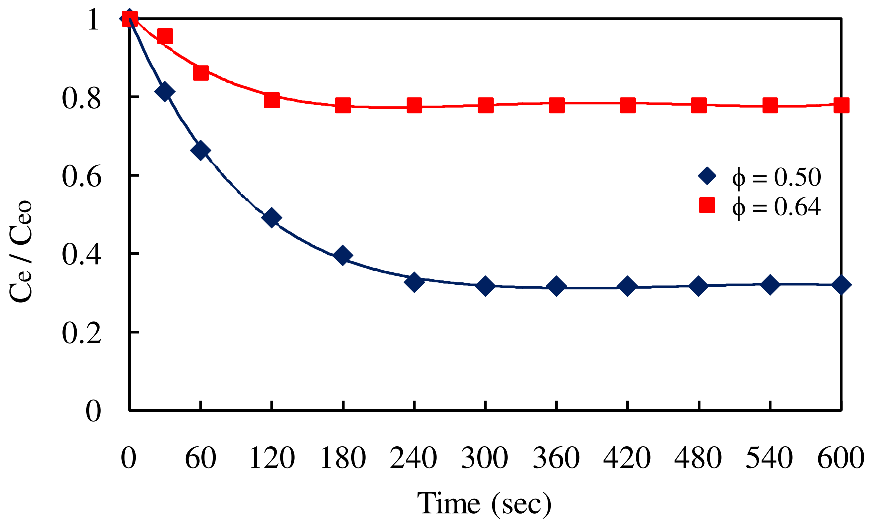


Fig. 4.30: Effect of internal phase volume fraction on rate of nickel extraction (W_{surf}=3 wt%, Cio=1.0 M, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

Fig. 4.30 shows the effect of variation of ϕ on the extraction of nickel, it is seen that there is considerable decline in the extraction rates with increase in ϕ. Increase in ϕ leads to an increase in the amount of stripping phase in the emulsion thereby increasing its extraction capacity. However, it also leads to an increase in the size of internal phase droplets in the emulsion, as a consequence the viscosity of the emulsion increases substantially as already reported in section 4.3.4. Hence, under the same agitation conditions a dispersion having large emulsion globule sizes is formed. The combined effect of large globule sizes and large internal droplet sizes results in decline in the mass transfer area and therefore the overall extraction rates. It is appropriate to note that increase in ϕ results in a decline in the membrane phase volume of the emulsion and also the amount of extractant in the system however, it also results in thinner membranes that result in lower diffusional resistances. Therefore, the issue is fairly complicated and exact reason for the decline in extraction rates cannot be pinned to any single effect rather the optimality of a particular value of ϕ appears to be sort of tradeoff between the contradictory effects.

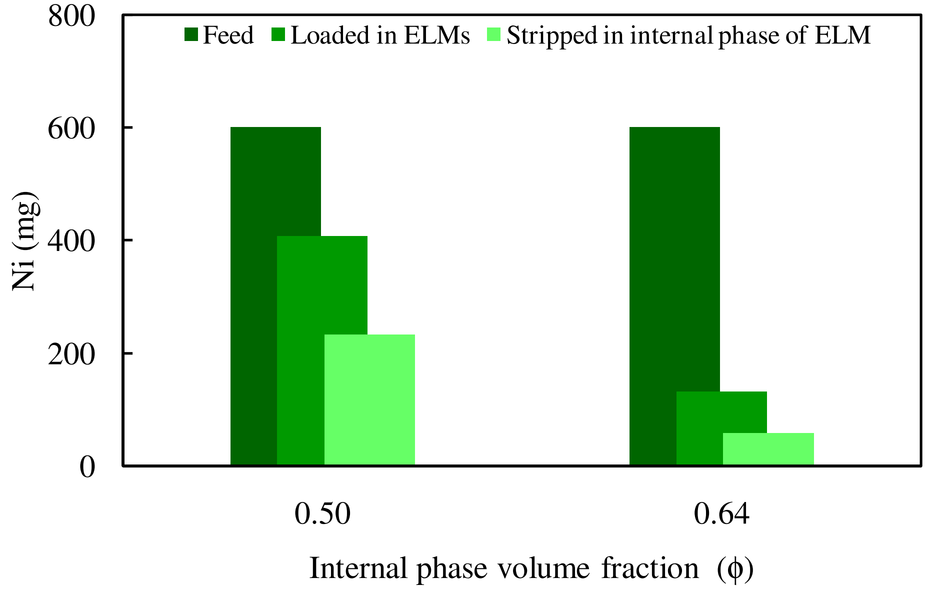


Fig. 4.31: Effect of internal phase volume fraction on stripping of nickel
(W_{surf}=3 wt%, Cio=1.0 M, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

The net effect is also reflected in the extent of nickel stripping by the internal phase shown in Fig. 4.31 which is about 44% of the total nickel loaded for the case of ϕ = 0.64. This low extent of stripping is primarily due to substantial reduction in the stripping surface areas and large increase in the viscosity of the emulsion that compensates for the reduction in diffusional path length.

4.9.4 Effect of carrier concentration (Cc)

Carrier concentration in the membrane phase has considerable influence on the overall extraction rates in ELMs. Effect of carrier concentration on nickel extraction was investigated at four LIX 84I concentrations in the membrane phase ranging from 5% (v/v) to 20% (v/v) using emulsions having ϕ=0.5 and Cio=1.0 M H_2SO_4. The treat ratio was maintained at 1:6 and initial nickel concentration Ceo was ~ 1000 mg/L (±30 mg/L). The effect of carrier concentration on the extraction of nickel from ammoniacal solution is shown in Fig. 4.32.

Extraction rates steadily increased with oxime concentration in the membrane phase. Carrier concentration of 5% (v/v) LIX 84I in the membrane phase resulted in linear decline in the nickel concentration in the feed over the entire span of the experimental run but increasing the carrier concentrations to 10% (v/v) led to a sharp decline in the nickel concentration in the feed phase within initial four minutes of contact with the ELMs, thereafter plateau in feed concentration was observed. Increasing the carrier concentration in the ELMs to 15% (v/v) showed similar initial trend although almost 15% enhancement in the extent of extraction at any time interval was recorded when compared with carrier concentration of 10% (v/v). Further increase in carrier concentration to 20% (v/v) in the first four minutes resulted in almost identical rates as observed with Cc=15% (v/v) but in the second half of the experimental run, the rate and extent of extraction both got enhanced resulting in almost 91.5% recovery of nickel about 8% more than the case with Cc=15% (v/v).

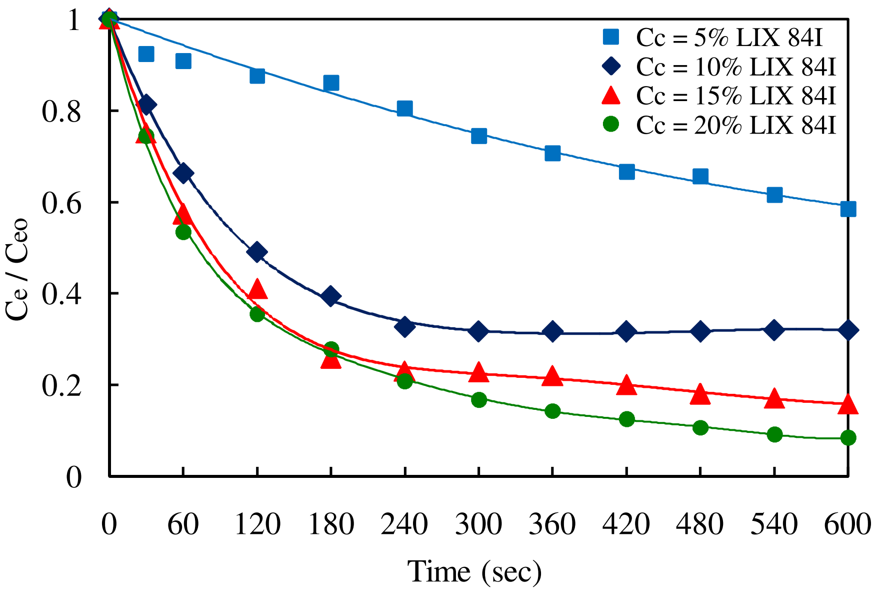


Fig. 4.32: Effect of carrier concentration on rate of nickel extraction
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.0 M, pH=8.1, Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

The distribution of nickel at the end of the run in the oil and aqueous phase of the emulsion is shown in Fig. 4.33, it is evident from the figure that in all the cases the extent of stripping is about 55% ± 2% of the nickel loaded in the emulsion. The increase in carrier concentration is primarily enhancing the capacity of the ELM to load more nickel and since there is greater amount of nickel in the oil membrane phase at higher carrier concentrations, more amount of nickel gets stripped. In such cases of high carrier concentration the internal phase droplets within the core of the globule also become effective in stripping the loaded nickel from the extractant complex.

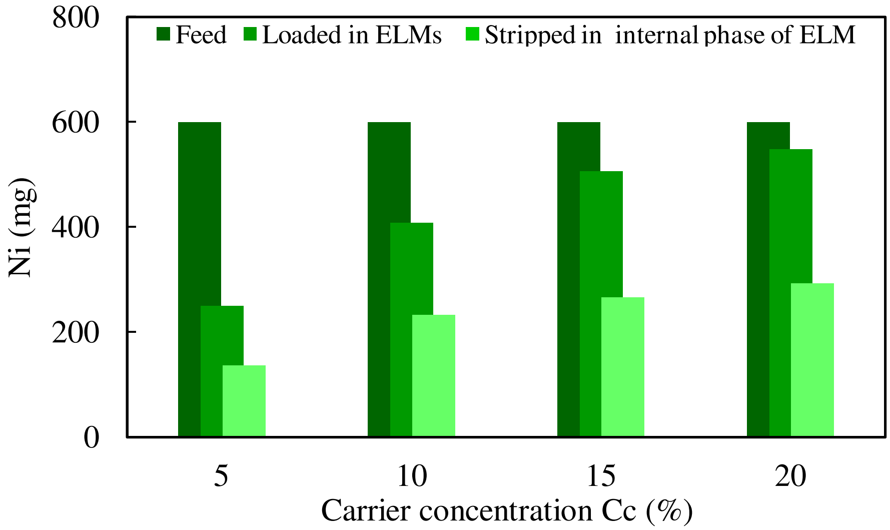


Fig. 4.33: Effect of carrier concentration on stripping of nickel
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.0 M, pH=8.1, Ceo=1000 mg/L, TR=1: 6, N=160 rpm).

4.9.5 Effect of initial feed concentration (Ceo)

The effect of Ceo on the rates of nickel extraction was investigated for nickel concentrations ranging from 500 mg/L to 1500 mg/L. The effect of Ceo was studied using emulsions containing 10% (v/v) as LIX 84I in the membrane phase with ϕ=0.5 and Cio=1.0 M. The extraction curves for feed concentrations of 500 mg/L, 1000 mg/L and 1500 mg/L of nickel in emulsion liquid membrane, as shown in Fig 4.34 where it is seen that almost 75% of initial nickel gets loaded at Ceo=500 mg/L, which reduces to 68% when Ceo=1000mg/L and further reduces to 42% when Ceo=1500 mg/L. In the later two cases for Ceo=1000 mg/L and Ceo=1500 mg/L the net amount of nickel loaded per 100 ml of emulsion turns out to be 408 mg and 398.7 mg respectively which are quite close, indicating that the membrane phase almost reaches a plateau with respect to its loading capacity for both these cases. Analysis of the internal aqueous phase of the emulsion, subsequent to emulsion breakage, also showed that the amount stripped in these cases were quite close 57% and 51% of the respective amount loaded.

The flux of the nickel carrier complex within the globules is dependent on the nickel concentration in the aqueous phase as well as on the carrier concentration in the oil membrane phase, when carrier concentration is held constant the flux depends largely on the initial metal complex and the permeation process is solely dependent on the diffusion of nickel species within the globule. Beyond a certain limiting metal concentration in the aqueous feed phase, the flux tends to level off indicating complete utilization of binding capacity available at the feed – globule interface. It also unambiguously points to the fact that under optimized conditions the loading capacity governs the extraction rates.

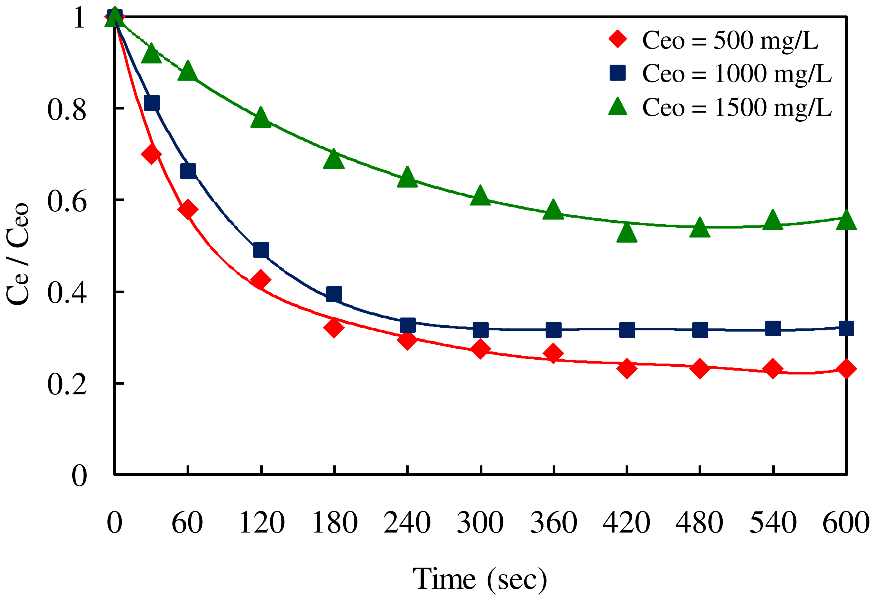


Fig 4.34: Effect of initial feed concentration on rate of nickel extraction
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.0 M, Cc=10% (v/v), pH=8.1, TR=1: 6, N=160 rpm).

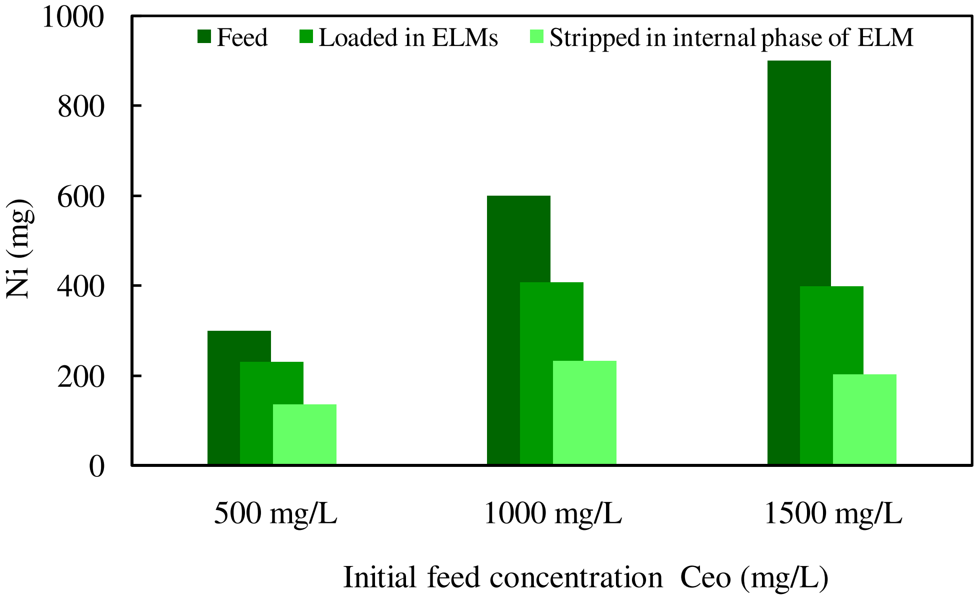


Fig 4.35: Effect of initial feed concentration on stripping of nickel
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.0 M, Cc=10% (v/v), pH=8.1, TR=1: 6, N=160 rpm).

The extent of stripping of the loaded nickel at the end of the run is shown in Fig. 4.35 it is clear that the extent of stripping is more or less similar in all 3 cases accounting for ~55% of the loaded nickel concentrations, irrespective of the initial feed concentration. These results suggest that the rate of stripping is inherently a slow process as proposed by investigators studying the kinetics of nickel extraction from LIX reagents. Therefore, the overall rates are all governed by loading pattern of the ELMs.

4.9.6 Effect of treat ratio (TR)

The treat ratio in an ELM extraction is the ratio of emulsion phase to feed phase and is a measure of emulsion holdup in the system. Increase in treat ratio functions on similar lines as that of increase in solvent amount in an extraction system. It always results in an increase in the extent and rates of extraction due to an increase in the amount of carrier as well as the amount of stripping phase in the system and consequently the mass transfer areas at both the external and internal interfaces. Extraction rates at three treat ratios of 1:8, 1:6 and 1:5 were obtained using emulsions containing 10% (v/v) LIX 84I as carrier and having an internal phase fraction ϕ=0.5 with initial feed concentration maintained at Ceo=1000 mg/L for all three cases.

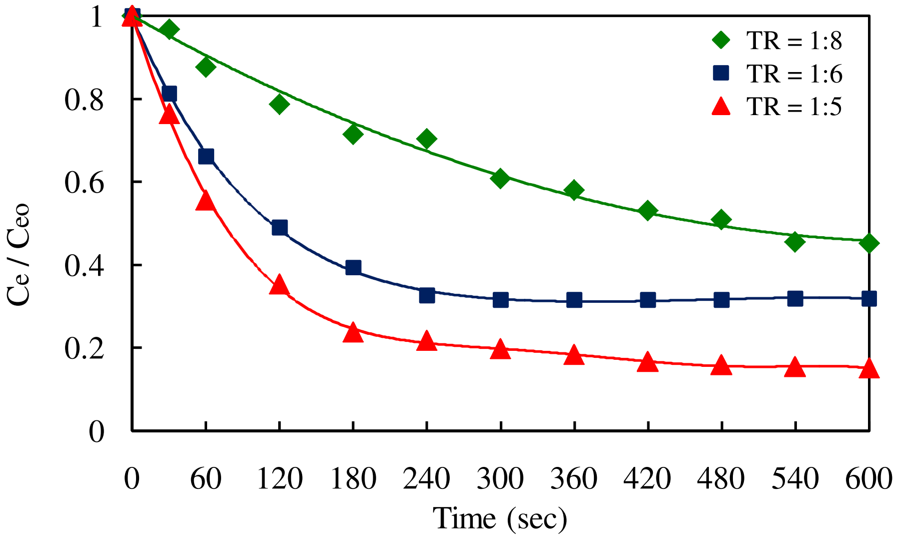


Fig. 4.36: Effect of treat ratio on rate of nickel extraction

(ϕ=0.5, W_{surf}=3 wt%, Cio=1.0 M, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, N=160 rpm).

Fig. 4.36 shows the extraction curves, it is seen that there is considerable difference in the rates and extent of extraction with varying treat ratios. Almost 85% of nickel gets extracted when TR=1:5 but only 55% of nickel is extracted for TR=1:8 for a contact time of 10 minute between emulsion and feed phase. The observed difference in extraction rates for lower treat ratio stem from the reduction in loading capacity of the oil membrane, due to reduction in the amount of carrier in the oil phase.

It is interesting to note that when TR is 1:6 the amount of emulsion volume in the system is only 25 ml more than TR 1:8 but the difference in extraction rates in the first half of the run is very large accounting for almost 40% (v/v) at four minutes of contact this difference later tapers down to settle at 15% (v/v) by the end of the run. This difference in rates due to variation of TR is contributed by numerous factors as discussed earlier but the dominant effect appears to be that of the carrier concentration in the system.

Since the carrier concentration also steps down by 25% when TR=1:8, it is easily figured out that amount of carrier in the system in this case is equivalent to a run with TR = 1:6 but having carrier concentration of 7.5 % (v/v) instead of 10 % (v/v). Comparing the extraction curve for TR=1:8 in Fig. 4.36 with the extraction curves in Fig. 4.32 showing the effect of carrier concentration makes this conclusion amply relevant.

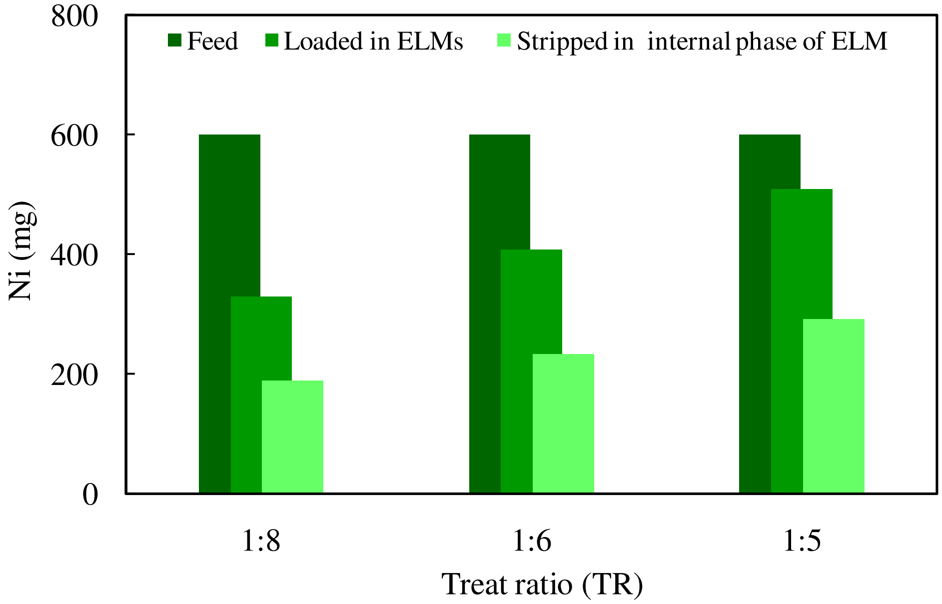


Fig. 4.37: Effect of treat ratio on stripping of nickel
(ϕ=0.5, W_{surf}=3 wt%, Cio=1.0 M, Cc=10% (v/v), pH=8.1, Ceo=1000 mg/L, N=160 rpm).

Similarly when TR=1:5, the amount of carrier in the system is about 20% more than the case when TR=1:6. The overall result also shows about 20% enhancement in the extent of nickel extraction at the end of the run. Interestingly the extent of extraction is almost as good as a run having TR=1:6 having 15% (v/v) carrier as observed by comparing the extraction curves of Fig 4.36 and Fig 4.32. From this result one can conclude that while factors such as mass transfer area etc., that increase with an increase in TR has a facilitating effect on the rates of extraction but the key parameter influencing the rates is the carrier concentration or in other words it is the loading of nickel in the oil membrane phase that dictates the extraction pattern.

Loading of nickel in the ELMs and its distribution at the end of the run between the stripping and oil membrane phase is shown in Fig 4.37 it is seen that almost 57% of the loaded nickel gets stripped in all three cases in the time span of the experimental runs.

4.10 Co-extraction of copper and nickel into ELMs

Co-extraction of nickel and copper from ammoniacal solutions was investigated using ELMs having W_{surf} =3wt%, ϕ=0.5, Cio=1.0 M, Cc=10% (v/v) LIX 84I in membrane phase, of membrane phase with treat ratio 1:6. The feed solutions were prepared by dissolving requisite amounts of copper sulphate, nickel sulphate and 50 gm/L ammonium sulphate in deionised water, thereafter the pH was adjusted to 8.1 using ammonium hydroxide. The effect of the emulsion parameters such as internal phase acid concentration, internal phase volume fraction, carrier concentration as well as the initial feed concentration of nickel and copper, on the rates of extraction of copper and nickel from the feed was investigated.

4.10.1 Effect of internal phase acid concentrations (Cio)

Two acid concentrations 0.5 M and 1.0 M were used in the internal phase of the W/O emulsions to evaluate the effect of stripping acid concentration on the extent and rates of copper and nickel extraction from feed solutions into ELMs. It is known that nickel gets stripped rather easily even with low acid strengths while copper gets stripped conveniently using acid strengths of 1.0 M and above. It was felt that low acid strengths would preferentially favor nickel removal while higher acid strengths would favor copper removal. This anticipation however is not observed in Fig. 4.38.

Extraction results shown in Fig. 4.38 are recorded for initial feed concentrations of 1000 mg/L of both nickel and copper. It is clear that the rate of extraction of both nickel and copper increased with stripping acid concentration from 0.5 M to 1.0 M. However, the rates of copper extraction were much faster than that observed for nickel. Moreover, while copper was almost quantitatively extracted in 3 minute into ELMs having Cio=1.0 M, even in the best case only 49% Ni was extracted in the contact time of 10 minutes with emulsions having Cio=1.0 M.

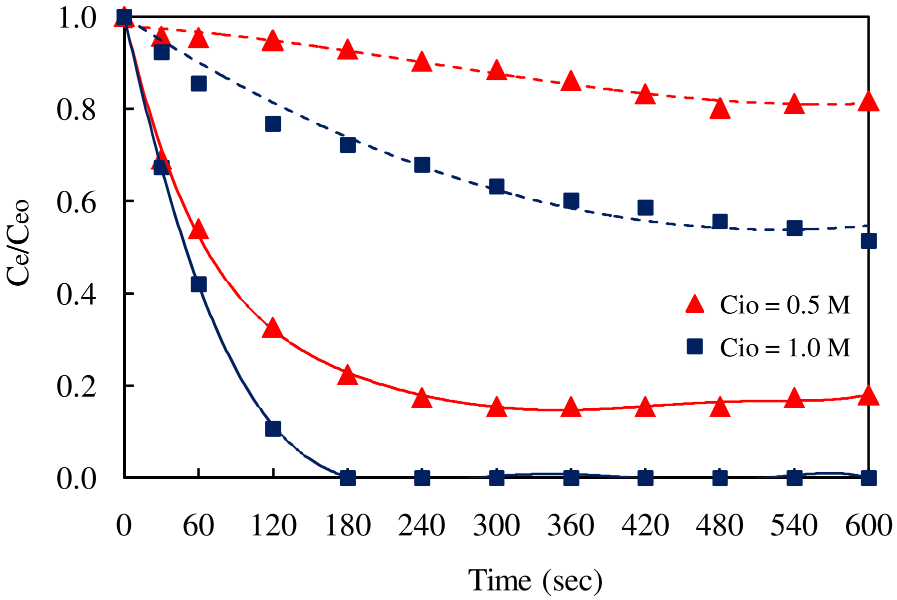


Fig. 4.38: Co-extraction of Cu–Ni into ELMs: effect of Cio (—— Cu, ---- Ni).
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Ceo=1000 mg/L, Cc=10% (v/v), TR=1:6, N=160 rpm).

Comparing Fig. 4.38 with Fig. 4.28 the effect of Cio on nickel extraction in the presence of copper is identified. There was significant decline in the extent and rates of nickel extraction in the presence of copper.

This decline is expected and attributed to the following two factors:-

LIX 84I which was used as the carrier in this investigation is primarily a copper extractant. The selectivity of LIX 84I for various metals follows the order Cu > Ni > Zn. Therefore, it is apparent that LIX 84I loads Cu preferentially and more rapidly than Ni. Secondly the rates of stripping of Cu appears to be faster than Ni at both internal acid concentrations as indicated by the histogram shown in Fig. 4.39 that presents the extraction and stripping profiles at both acid concentrations.

It is very likely that copper ions, which complexes more rapidly and preferentially with LIX84I, diffuses rapidly inside the ELM globules and encounters the peripheral internal droplets where the Cu gets stripped and depletes the acid in those droplets. The loaded nickel complex has to diffuse much deeper within the emulsion globule to encounter the stripping reagent to get stripped. Hence the aspect of enhanced diffusional path length also contributes to the decline in observed extraction rates for nickel in the presence of copper.

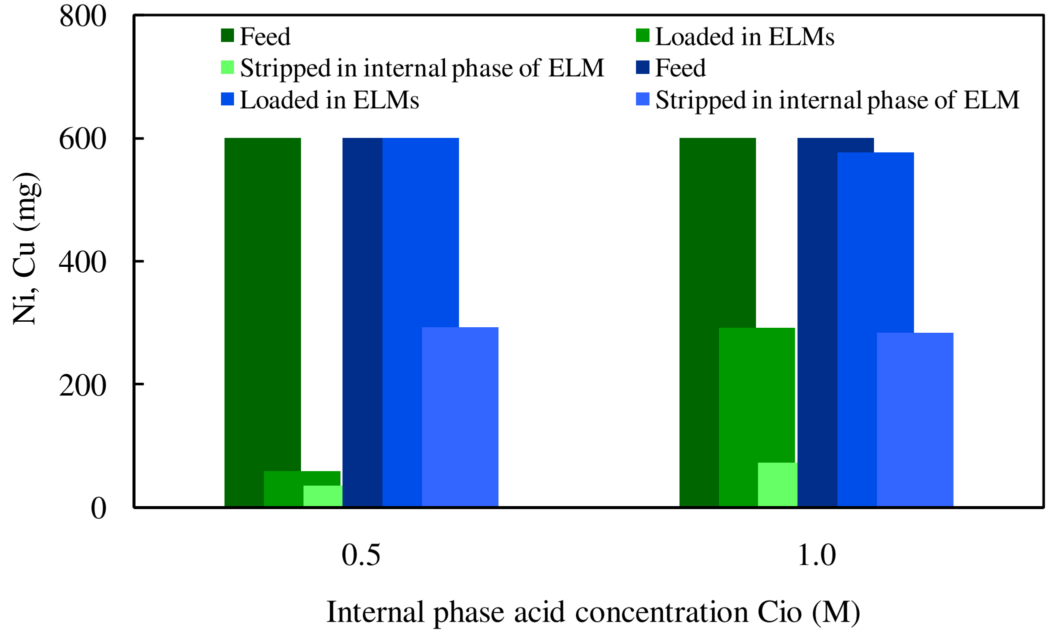


Fig. 4.39: Simultaneous stripping of Cu–Ni into ELMs: effect of Cio (🟦 Cu, 🟩 Ni)
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Ceo=1000 mg/L, Cc=10% (v/v), TR=1:6, N=160 rpm).

4.10.2 Effect of initial feed concentration (Ceo)

Variation of copper and nickel in the initial feed concentration were explored to gain understanding of the pattern of simultaneous extraction of both the metals in ELMs from fairly concentrated feeds. The idea was to test the efficacy and stability of the ELMs to extract such feeds and also to identify restrictions – if any high metal concentrations imposed on the uptake of metals by the ELMs. The copper concentration in these feeds where widely varied in the range of 1000 – 5760 mg/L while that of nickel was moderately varied in range of 1000 – 1570 mg/L.

The ELMs used had Cio=1.0 M while all other conditions remained identical. Extraction results are shown in Fig. 4.40 For all three cases copper extraction was much faster than nickel extraction, almost quantitative removal of copper took place within seven minute at maximum copper concentration of 5760 mg/L while a maximum of 34% nickel removal took place when initial nickel concentration of 1570 mg/L in the same time duration.

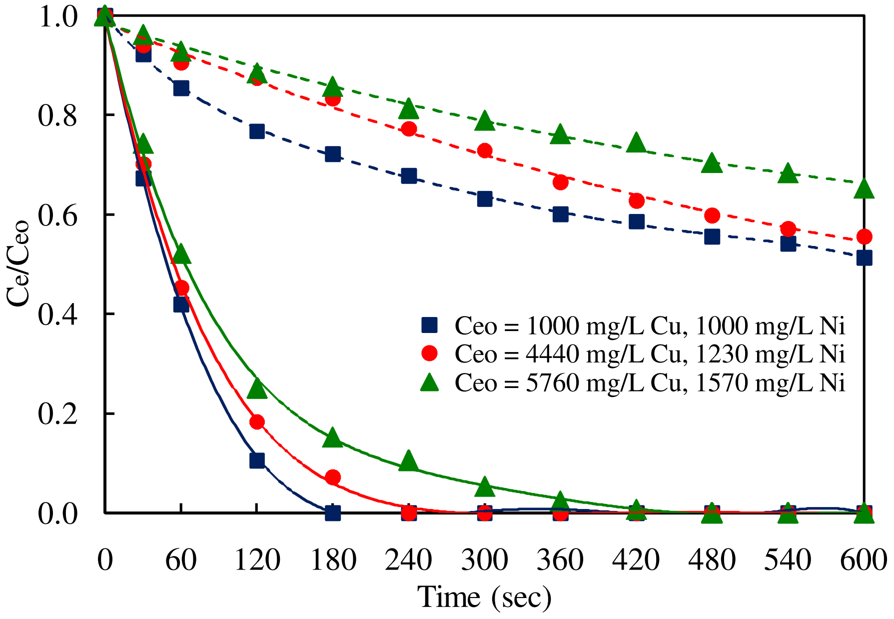


Fig. 4.40: Co-extraction of Cu–Ni into ELMs: effect of Ceo (—— Cu, ---- Ni). (ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.0 M, Cc=10% (v/v), TR=1:6, N=160 rpm).

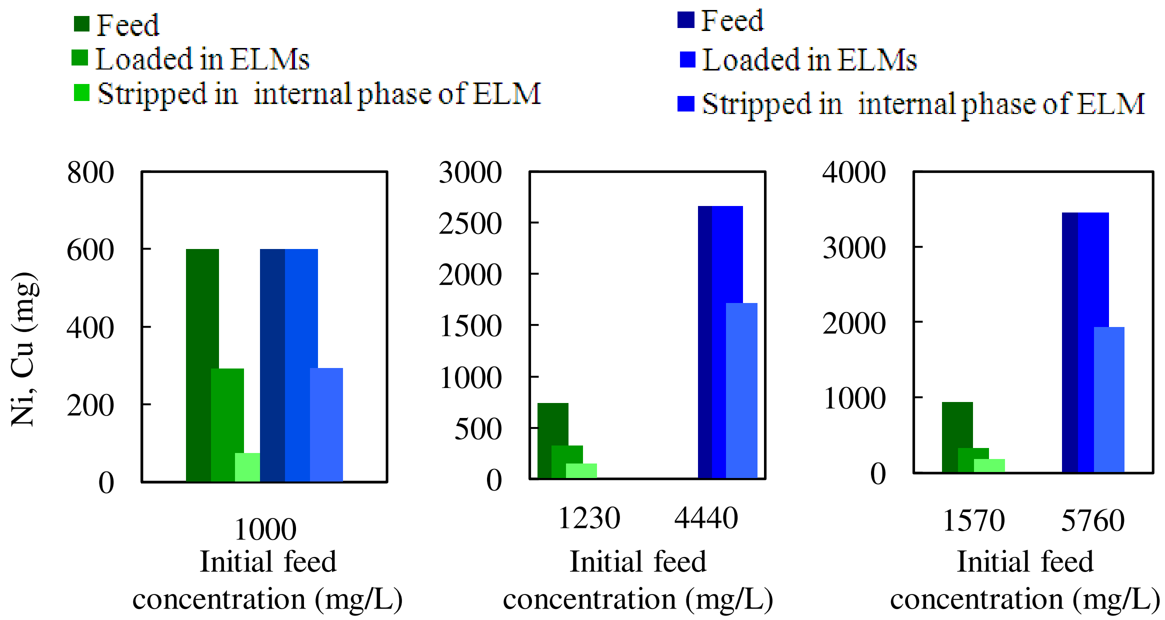


Fig. 4.41: Simultaneous stripping of Cu–Ni into ELMs: effect of Ceo (🟦 Cu, 🟩 Ni) (ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.0 M, Cc=10% (v/v), TR=1:6, N=160 rpm).

This pattern is attributed to the same factors discussed in the previous section, copper gets loaded faster; this induces a large flux of copper-oxime complex directed inwards within the emulsion. All peripheral internal phase droplets are depleted of their acid content to strip the copper hence nickel has to diffuse deeper to get stripped. The slow rate of extraction observed for nickel is additionally contributed by the slow stripping rates of nickel in ELMs. The histogram shown in Fig. 4.41 bears testimony to these ideas.

4.10.3 Effect of internal phase volume fraction (ϕ)

The effect of the internal phase volume fraction on the rates of simultaneous extraction of copper and nickel is shown in Fig 4.42. It is observed that the extraction rates of both metals are considerably faster when ϕ=0.5 in comparison to ϕ=0.64. Decline in extraction rates stems from a number of effects primarily the increase in the internal phase volume causes a decline in the membrane phase to the extent of 32% and correspondingly a similar decline in the extractant content in the system this leads to a rapid decline in loading capabilities of the ELMs. This effect is augmented by a shift in the internal droplet size distribution to larger sizes as shown in Fig. 4.7. On an average it is found that the Sauter mean diameter shifts from 2.72 μm for ϕ=0.5 to 10.75 μm for ϕ=0.64, large internal droplet sizes results in lower internal surface areas in ELMs having ϕ=0.64 that results in slow rates of stripping. Therefore an overall decline in the extraction rates is observed.

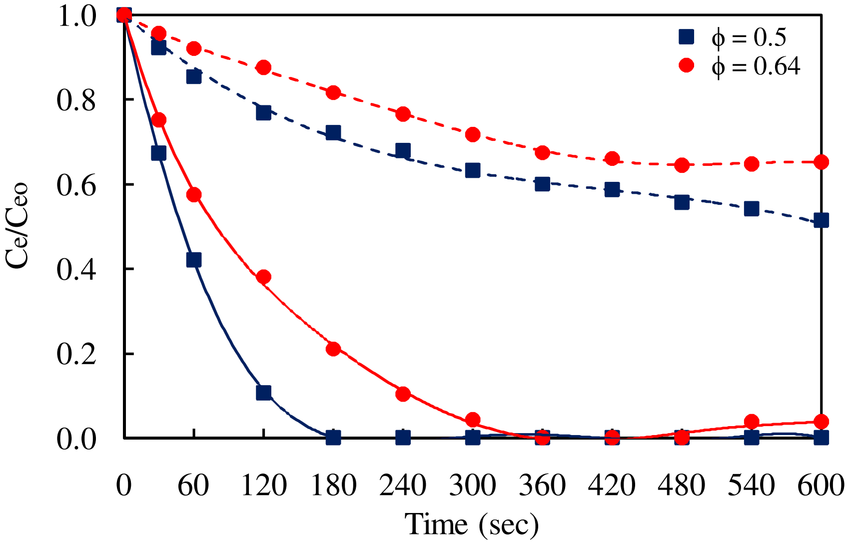


Fig. 4.42: Co-extraction of Cu–Ni into ELMs: effect of ϕ (—— Cu, ---- Ni). (Cio=1.0 M, W_{surf}=3 wt%, pH=8.1, Cc=10% (v/v), TR=1:6, N=160 rpm).

Analysis of the internal phase of the ELMs after emulsion breakage at the end of the experimental run reveals very interesting insight on the overall dynamics of the process. From Fig. 4.43 it is observed that with ϕ=0.5 all of the copper in the feed mixture is loaded in the emulsion but only half of it is stripped. When ϕ=0.64 nearly 95% of the feed copper is loaded in the ELMs and again almost half of it is stripped.

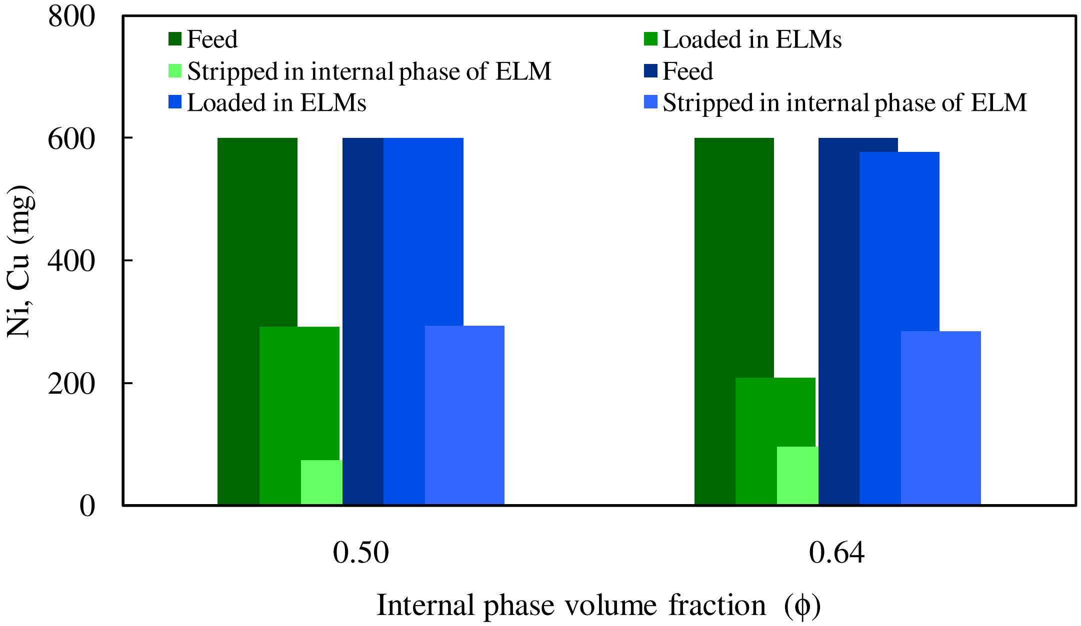


Fig. 4.43: Simultaneous stripping of Cu–Ni into ELMs: effect of ϕ (🟦 Cu, 🟩 Ni)
(Cio=1.0 M, W_{surf}=3 wt%, pH=8.1, Cc=10% (v/v), TR=1:6, N=160 rpm).

The effect of ϕ is not felt prominently in the case of copper extraction but during Ni extraction it is found that ELMs having ϕ=0.5 load only ~ 50% of the Ni from the feed and of it just 25% is stripped. While with ELMs having ϕ = 0.64 only 36% of the initial Ni in feed is loaded. Thus we find that with a 32% decline in the extractant content in the system there is a corresponding 27% decline in the Ni extracted. Hence, a close correlation between the extractant content in the system and amount of Ni extracted gets established. It is surprising that contrary to expectations that the amount of Ni stripped is almost 50% of that extracted such large amount of stripping is attributed to the large internal phase present within the ELMs that make available a lot of acid for stripping the Ni from loaded complex.

4.10.4 Effect of carrier concentrations (Cc)

Carrier concentration in the membrane phase has a dominating influence on the overall extraction rates of nickel in ELMs. Effect of carrier concentration on extraction of copper and nickel mixture was investigated at three LIX 84I concentrations in the membrane phase ranging from 10% (v/v) to 20% (v/v) using emulsions having ϕ=0.5 and Cio=1.0 M H_2SO_4.

The treat ratio was maintained at 1:6 and initial concentrations of both copper and nickel was nearly 1000 mg/L. The effect of carrier concentration on the extraction of copper and nickel mixture from ammoniacal solution is shown in Fig. 4.44.

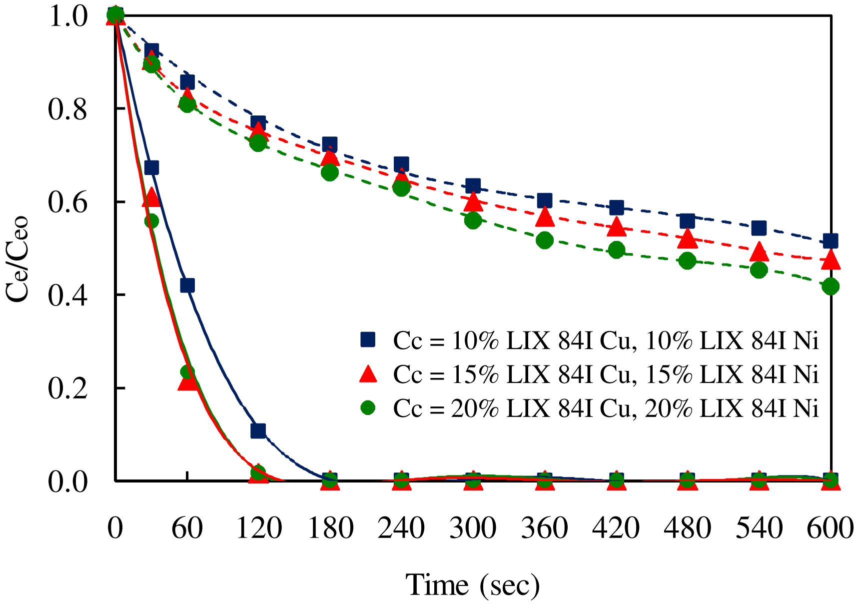


Fig. 4.44: Co-extraction of Cu–Ni into ELMs: effect of Cc (—— Cu, ----- Ni).
(ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.0 M, TR=1:6, N=160 rpm).

Extraction rates of copper from the feed mixture were identical for emulsions containing 15% (v/v) and 20% (v/v) oxime concentration in membrane phase while they were marginally slower for Cc=10% (v/v). However, quantitative extraction of copper was observed in these extractions but at different time intervals.

Due to preferential complex formation of LIX 84I with copper its uptake by the ELM is very rapid and as a consequence the rate of uptake of nickel that is relatively slow gets even more retarded in the presence of copper. It can be seen from Fig 4.44 that only after copper is quantitatively loaded in the ELMs the rate of nickel loading gets enhanced for Cc of 15% (v/v) and 20% (v/v) LIX 84I while for Cc=10% LIX 84I even that is not observed.

The decline in the rates of Ni extraction from mixed solute system can largely be attributed to the shortage of free carrier within the ELM system available to bind with nickel. This becomes amply clear from Fig. 4.45 that shows almost ~ 50% of the loaded Cu remains non-stripped at the end of the run in all three cases. Thereby implying that considerable amount of extractant remains bound with copper and is not free for loading nickel, this shortage of free extractant results in decline in nickel loading. It is seen from Fig. 4.45 that the amount of Cu stripped has a good correlation with the amount of Ni loaded.

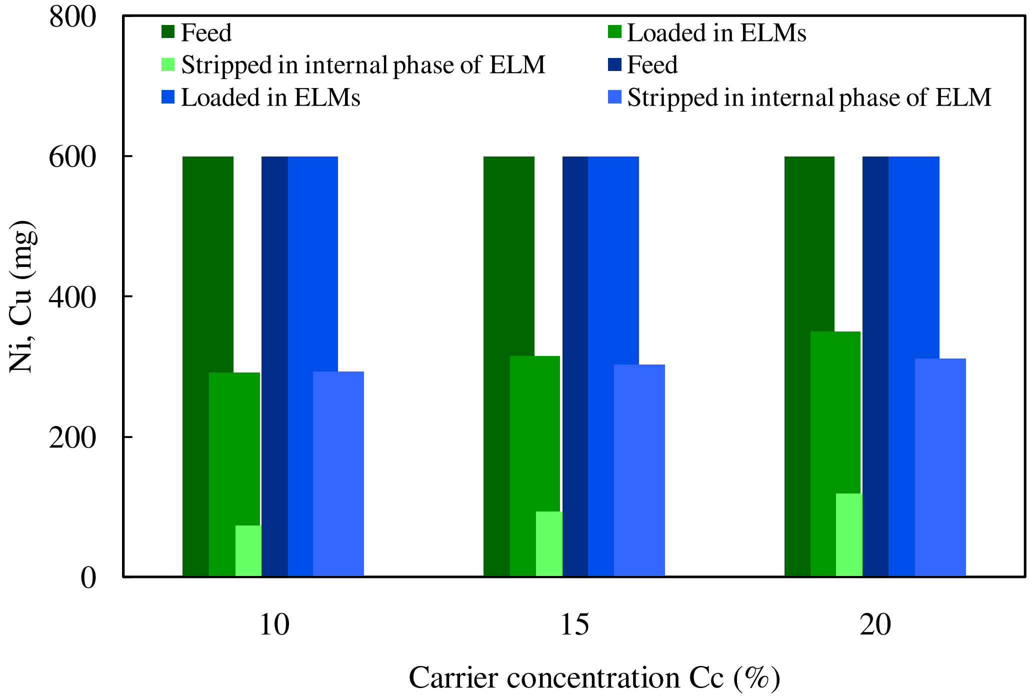


Fig. 4.45: Simultaneous stripping of Cu–Ni into ELMs: effect of Cc (🟦 Cu, 🟩 Ni) (ϕ=0.5, W_{surf}=3 wt%, pH=8.1, Cio=1.0 M, TR=1:6, N=160 rpm).

These results bring home another point and that is the strong complexation of Cu with LIX 84I does not get displaced easily. Hence the stripping of Cu is slow, particularly with acid of 1.0 M concentration. If higher acid strength had been used then it is likely that Cu could have got stripped to a greater extent resulting in more amount of free extractant to load Ni but at the same time Ni stripping would have been even more retarded.

Table 4.3 details the quantitative aspects of the Cu–Ni separation using ELMs. It is distinctly observed that ELMs with LIX 84I show a preference for the selective removal of copper from Cu–Ni mixtures. Other aspects including stripping kinetics of copper and nickel, physicochemical features such as diffusion of the oxime complex within the emulsion globule etc all get completely masked by the affinity of the oxime for copper. The separation factor $\beta_{(Cu/Ni)}$ obtained at time duration of 10 minutes, corresponding to onset of maximum copper removal, ranged from 1.41 to 2.91 is shown in Table 4.3.

Table 4.3: Extraction and stripping of Cu–Ni in ELMs

	Initial feed conc. (mg/L)		Net amount in feed (mg)		Amount loaded in ELM (mg)		Amount stripped in internal phase of ELM (mg)		Separation factor (β)
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	-------
a	1000	1000	600	600	600	291.6	293	73.5	1.41
b	4440	1230	2664	738	2664	327	1716	152.18	1.51
c	5760	1570	3456	942	3456	326	1935	183.6	2.91

4.11 Conclusions

The significant conclusions drawn from this investigation on the ammoniacal extraction of copper, zinc and nickel and co-extracton of copper- zinc and copper-nickel reveal the following:-

Copper, zinc, nickel and their mixtures were extracted from ammoniacal-ammonium sulphate solutions into ELMs using the ketoxime LIX 84I as carrier. Although LIX 84 I is primarily a strongly chelating copper extractant it could be effectively used not only for copper extraction but for zinc and nickel extraction as well, pH 8.1 was preferred for extraction because it not only resulted in fast extraction rates but also because free ammonia in the feed was at a very low level, inhibiting ammonia transport through the membrane.

Ammoniacal extraction of copper using LIX 84I was fast even by ELM standards. Extraction runs were almost over in 3 min of contact between the membrane and feed phase. Loading of copper in the membrane phase was almost instantaneous. Loading was strongly influenced by carrier concentration. In almost all cases copper loading in the membrane phase governed the rate of extraction. Other physico-chemical factors like stripping, diffusion of the oxime complex, globule size and drop size distributions were delegated to secondary importance in the overall extraction process. Attempts to enhance extraction capacity of emulsions by increasing the stripping phase volume fraction ϕ did not yield positive result. It was found that increase in carrier concentration and emulsion hold up was always favorable for copper extraction. In most extractions, quantitative removal was observed in 2 min of contact between the emulsions and feed.

Prior to zinc extraction using ELMs the loading and stripping behavior of zinc in kerosene containing LIX84I was performed, the results indicate that stripping was slower in comparison to loading. Experiments on the simultaneous extraction of copper and zinc and their stripping indicate that zinc loads in the oil phase to a greater extent in the presence of copper. Zinc strips faster than copper from the oil phase when the zinc concentration is comparable or more than copper.

Investigations with ELMs indicate that zinc extraction rates are considerably influenced by the emulsion parameters ϕ, Cio and Cc. An increase in ϕ had a deleterious effect on the metal extractions, optimal values of emulsion parameters were Cio=1.5 M, Cc=10% (v/v) LIX 84I and ϕ=0.5.

Increase in zinc concentrations in the feed resulted in larger zinc uptake by the ELMs. However, zinc stripping was slow, hence considerable amount of zinc was retained in the membrane phase, particularly when zinc uptake in the ELMs was large. The zinc stripping rate was found to be constant in the time span of the experiments.

Simultaneous extraction of copper and zinc using ELMs indicates that the overall copper extraction rates are much larger than zinc. Loading of copper dictates the separation. ELMs with LIX 84I show preference for selective removal of copper from zinc with separation factor β(Cu/Zn)=3.5. These ELMs could be used for treating the ammoniacal wastewaters obtained from PCB manufacturing units containing Cu–Zn mixtures.

Extraction of nickel from ammoniacal solutions introduced a new dimension in these investigations because of disintegration of the emulsion and assessing the amount of Ni stripped in the internal phase of the emulsion. pH 8.1 was found more suitable than pH 7.0 because greater extent of Ni stripping took place at pH 8.1.

Ni extraction was most favored when internal phase acid concentration was 1 M. Increase in ϕ was deleterious for the extraction with the amount of nickel extracted and stripped declining sharply at $\phi = 0.64$ in comparison with $\phi = 0.5$. The magnitude of nickel extracted increased with the carrier concentration in the emulsion indicating that loading patterns govern the overall extraction process; the same claim was reiterated by the investigations detailing the effect of initial feed concentrations and the treat ratio. Loading of nickel governs the overall process and the amount of nickel stripped in all cases was ~55 % of the amount extracted.

The co-extraction of copper and nickel using LIX 84I from ammoniacal media indicates that internal phase acid strength of 0.5M is inadequate for stripping of copper as well as nickel from membrane phase a minimum acid strength of 1 M acid was appropriate. The rate of copper extraction was much greater than the rate of nickel extraction. In the experimental range of concentrations investigated copper could be quantitatively loaded in the emulsion even when its concentration was very large. Nickel loading declined in the presence of copper further copper stripped to a far greater extent in the internal phase of the emulsion in comparison to nickel.

Increase in ϕ was deleterious to nickel extraction but did not affect the copper extraction and stripping significantly. Increase in carrier content increased the rates of copper and nickel uptake by the ELMs but did not affect the net copper uptake but marginally improved the nickel uptake. It was interesting to find that the amount of copper stripped in the internal phase was equivalent to the amount of nickel uptake by the ELMs.

It was found that ELMs loaded with LIX 84I had the efficacy of removing nickel as well as mixtures of copper and nickel from aqueous ammoniacal media. Further, they could be used for selective removal of copper from Cu–nickel mixtures in ammoniacal media. The separation factor favoring copper increases with increasing initial copper concentration in the feed and had a maximum value of 2.91 in the concentration range studied in the experiments.

CHAPTER 5
EXTRACTION OF ZINC FROM SULPHATE SOLUTIONS

5.1 Introduction

The extraction of heavy metals from sulphate solutions has been widely investigated even with ELM technologies. Although major focus has been on the removal and recovery of copper from sulphate liquors but recovery of other transition metals such as Ni, Co, Fe, Cr, Zn, etc from sulphate solutions have also have been explored. The first commercial scale plant based on ELM technology was built in the Austrian viscous and rayon industries by Lenzin A. G. for treating wastewater coming from rayon spin bath. The wastewater contained 500 mg/L of Zn which was selectively separated from Ca to obtain residual solution containing 3 mg/L of Zn. Initially a pilot plant having capacity of 1 m^3/hr of wastewater was operated for more than two years to optimize the various plant parameters prior to construction of actual plant having capacity of 75 m^3/hr (Draxler *et al.* 1988).

While Zn removal from waste streams have demonstrated the potential of ELM as a separation technique and it also promises wider proliferation of this technology, but some irritants remain that need to be resolved to reinforce this technique. The major problem in commercial Zn removal by ELMs technologies happens to be the choice of a suitable extractant. Usually D2EHPA is used for the extraction of Zn in hydrometallurgical industries and is reported to be a good extractant for zinc in the pH range 2.5 – 3.5 (Rice and Smith 1975), but D2EHPA extracts a sizeable amount of Ca and other metal cations as in the CENIM-LNETI process. The order of extraction of metal ions from sulphate solutions by D2EHPA is reported to be in the order Fe(III) > Zn > Ca > Mn > Cu > Mg > Co >> Ni (Cole and Sole 2002) indicating that D2EHPA is not selective to the extraction of Zn in the presence of Ca.

Phosphoric acid derivatives such as PC 88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and CYANEX 272 ((di-2, 4, 4, - trimethylpentyl) phosphinic acid), CYANEX 302 (bis(2, 4, 4 - trimethylpetyl) monothiophosphinic acid) and CYANEX 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) have been successfully used as extractant for various metal ions from sulphate solutions including zinc and manganese.

(Cole and Sole 2002) observed that the order of extraction of common cations with CYANEX reagents is as follows:

CYANEX 272	Fe(III) > Zn > Cu > Mn > Co > Mg > Ca > Ni.
CYANEX 302	Cu > Fe(III) > Zn > Co > Mn > Ni >>> Mg ~ Ca
CYANEX 301	Cu > Zn > Fe(III) > Co ~ Ni >>Mn >>> Mg ~ Ca

The extraction order of these three CYANEX extractants indicate that they have considerable selectivity of Zn over Ca, similar is the case with PC 88A. It appears from the investigations of Marr and coworkers (Draxler and Marr 1986) that although CYANEX 272 and PC 88A were tried out as extractants in the Lenzing plant but these extractants did not qualify due to poor extraction efficiency at the specified pH value. Eventually DTPA (bis(2-ethylhexyl)dithiophosphoric acid) was used as the extractant that has an extraction order of: - Ag > Pb ≅ Cd > Fe(III) > Zn ≅ Ni >> Ca.

Although DTPA is a strong extractant for many cations but it is rarely used for the solvent extraction of metals due to very slow kinetics of the stripping reaction. Reis *et al.* (2004) also investigated the recovery of Zn from industrial effluent using monothioDEHPA and dithioDEHPA in ELMs. They observed that dithioDEHPA gave very stable complex with divalent metal cations that accumulated in the membrane phase and was very difficult to strip. With monothioDEHPA although the stability of complexes was not as problematic as in the previous case, but it was difficult to attain a specified level of separation of Zn primarily due to breakup of emulsion during extraction processes. Further, it was observed that with both the extractants to avoid emulsion breakage it was necessary to reduce the contact time of process, which could be done only by increasing the internal phase acid concentration. This resulted in large swelling of the emulsion due to osmotic flow of the diluents (water).

In view of the promise of commercialization of ELM technology for Zn removal as well as the wealth of existing information, a systematic investigation was planned for Zn extraction using major organophosphorous extractants such as D2EHPA, PC 88A and CYANEX 302 with the objective of attaining nearly quantitative extraction at reasonable rates.

5.2 Extraction behavior of zinc with organophosphorous extractants

The family of organophosphorous extractants is extensively used in the hydrometallurgical industry for separation and purification of transition metals, rare earths and other heavy metals. D2EHPA is a phosphoric acid known since 1949, PC 88A is a phosphonic acid introduced by Daihachi Chemical Industry Co in August 1978 (Preston 1982). CYANEX reagents based on phosphinic acids were developed by American Cyanamid Co around 1980.

According to the Hard – Soft – Acid – Base concept, the complexation of a soft Lewis acid such as Ni, Cu, and Zn with a soft Lewis base should occur with high selectivity. The donor atoms of Lewis bases have electronegativities in the order S > Br > N > Cl. Sulfur substitution of organophosphorous reagents therefore are beneficial to the extraction of these metal ions (Sole and Hiskey 1992). CYANEX 302 used in this investigation is a monothio substituted phosphinic acid.

The mechanism of extraction involving acidic organophosphorous extractants such as D2EHPA, PC88A, CYANEX 302 are complicated to describe, since the species extracted and the nature of metal complexes formed depends on many factors such as type of metal cation and its concentration, equilibrium pH of aqueous phase, extractant concentration, solvent phase properties that determine the formation of dimers etc. in the organic phase. It is known that D2EHPA exists in a dimeric form in kerosene (Huang and Juang 1986), same is the case with PC 88A in non polar aliphatic solvents (Kasaini *et al.* 1998).

During the extraction reaction, the organophosphorous acids such as D2EHPA principally act as cation exchangers. The oxygen atom of the phosphoryl group P=O coordinates with the ions extracted by forming chelating products; it also plays an important role when the extraction is carried out starting from the strongly acidic aqueous solutions, since D2EHPA behaves like solvating agent. The extraction of zinc by D2EHPA in kerosene is described by the following reaction:-

$$Zn_{aq}^{2+} + 1.5\ (H_2A_2)_{org} \rightarrow ZnA_2(HA)_{org} + 2H_{aq}^{+} \qquad \ldots\ldots (5.1)$$

The extracted zinc is solvated by 1.5 molecules of D2EHPA monomer and the extracted complex of zinc with D2EHPA is a monomeric compound where the monomers are not associated with each other (Sainaz-Diaz *et al.* 1996, Mellah and Benachour 2006).

Extraction of metal ions by cation exchange type extractants such as PC 88A involve a sequence of steps such as distribution of extractant between organic and aqueous phase, dissociation of extractant as cationic (H^+) and anionic (A^-) ions, complex formation between the extractant (A^-) ion and the metal in the aqueous phase and the transfer of metal complex from the aqueous to organic phase (Park *et. al* 2006). This necessitates that these class of compounds have at least sparing solubility in aqueous phase, which is in contrast to the water insoluble hydroxyoximes that bind metals by chelating at the oil-water interface.

The general reaction that describes the complexation of zinc by organophosphorous extractants such as D2EHPA, PC 88A, CYANEX 302 is expressed by the following equation:-

$$Zn^{2+}{}_{(aq)} + m\, HA_{(org)} \rightleftharpoons ZnA_2\,(m\text{-}2)\, HA_{(org)} + 2H^+ \qquad \text{.....(5.2)}$$

where HA represents the acidic extractant molecule and m varies from 2 to 4.

Prior to their use in ELM systems for Zn extraction, the extraction pattern of these extractants in acidic sulphate media was investigated by contacting a known volume of Zn sulphate solution at constant temperature with an equal volume of organic phase that was a mixture of kerosene and extractant at a definite pH till equilibration was attained. Equation (5.2) suggests that as extraction proceeds there will be a drop in solution pH due to release of two H^+ ions, hence, to maintain the pH at a fixed value the pH of the mixture was raised to its specified value by adding alkali to the solution. When no further change in solution pH took place on contacting the oil and aqueous phase, equilibration was attained. Thereafter, the oil and water phases were separated and metal content in the aqueous phase was analyzed by AA spectrometer, the metal content in oil phase was determined by material balance. Such data of extraction was determined for the three extractants over a wide range of pH values at room temperature of $30^0 \pm 1^0$C, carrier concentration of 10% (v/v) and initial zinc concentration 1000 mg/L (± 20 mg) Fig. 5.1 shows the equilibrium plot generated for the three extractants.

From the Fig. 5.1 it is easy to make out that the major difference in extraction patterns of these three extractants manifest at low pH values. Above a pH value of 2.5 there is marginal difference in the extraction patterns of the three extractants. CYANEX 302 needs higher pH values than D2EHPA and PC 88A to extract zinc ions, because phosphinic acid derivatives are weaker acids than the phosphoric and phosphonic acid, with the pK_a value of the extractant in the order D2EHPA < PC 88A < CYANEX 302. The pK_a values in water being 1.27 and 5.63 for D2EHPA and CYANEX 302 respectively.

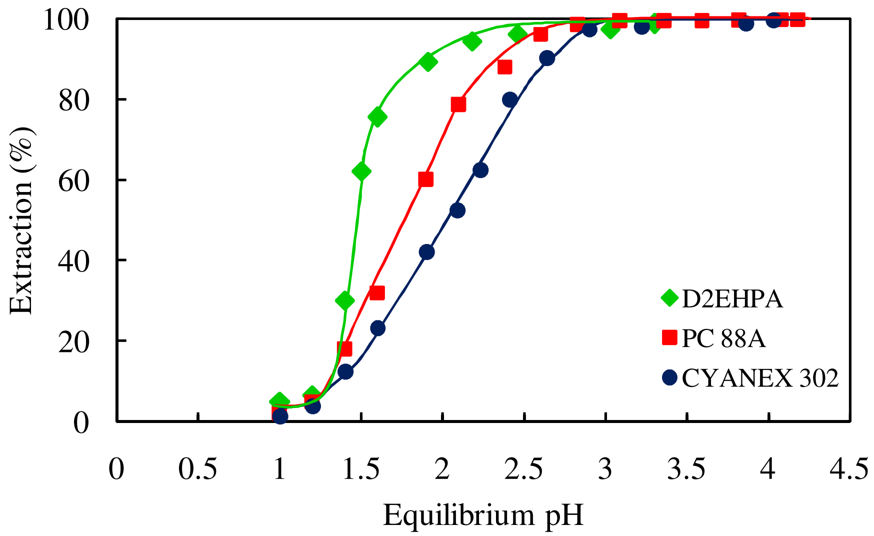


Fig. 5.1: Extraction patterns of zinc using D2EHPA, PC 88A and CYANEX 302 in kerosene

Building up on the extraction patterns of the three extractants and their bonding pattern observed using IR spectroscopy. The efficacy of the actual extraction behavior of the three phosphoric acid extractants in emulsion liquid membrane system for extraction of zinc from sulphate media was investigated. The range of parametric variations investigated is reported in Table 5.1. Further a synergy between the extractants for zinc extraction was also explored and is reported in the subsequent sections.

Table 5.1 Range of parametric variations studied for extraction of zinc into ELMs using organophosphorous extractants:

W_{Surf} =3 wt%, Speed of agitation N=150 rpm						
Variants ↓	Cio (M)	ϕ	Cc % (v/v)	TR	Ceo (mg/L)	pH
ϕ	1.5	0.5, 0.555, 0.6, 0.64	10	1:6	1000	4.5
C_{io}	0.5, 1.0, 1.5, 2.0	0.5	10	1:6	1000	4.5
C_c	1.5	0.5	2, 5, 7.5 10, 15	1:6	1000	4.5
pH	1.5	0.5	10	1:6	1000	1.5, 2.5, 3.5, 4.5
C_{eo}	1.5	0.5	10	1:6	500, 1000, 2000, 3000	4.5
TR	1:5	0.5	10	1:15, 1:10, 1:6, 1:5	1000	4.5

5.3 Zinc extraction using D2EHPA into ELMs

The extraction of zinc from aqueous sulphate solutions alone or its coextraction with other metals such as cadmium, copper etc using D2EHPA has been extensively studied (Mellah and Benachour 2006, Huang and Juang 1986). However, zinc extraction using D2EHPA in emulsion liquid membranes has been explored by only by Raghuraman *et al.* (1994), Carvalho and coworkers (Carvalho and Reis 1993, Carvalho, Reis and Bart 1999) and Fouad (2008). It is note worthy that focus of the first two investigators was on modeling of these systems and that of the third investigator was on copper – zinc separation hence effect of only limited number of process parameters on extraction rates were investigated. Further these investigations reported severe membrane breakage at almost all stirring speeds. The objective of the current investigation was to explore the limits of extraction space using fairly stable emulsion membranes and identify the critical features of this separation.

5.3.1 Effect of process parameters

Effect of pH

The pH of the feed phase always has profound influence on the extraction behavior. It is well known that D2EHPA is strong zinc extractant. Fig. 5.2 shows the effect of initial feed phase pH on extraction of zinc using emulsions having specifications mentioned in Table 5.1. At pH 1.5, the maximum extent of zinc recovery was ~ 65%, although from Fig 5.1 one can make out that at equilibrium pH of 1.5 the extent of Zn removal is about 50%. One has to note that the pH reported in ELM extraction is the initial pH and not equilibrium pH. The pH of feed solution during ELM extraction of Zn would constantly decline during the entire period of extraction on account of proton release in the feed solution due to uptake of Zn as shown in Equation 5.2.

The total zinc extraction observed during the entire period of run is the cumulative of extraction taking place at pH values of 1.5 and lower. Under no circumstance the amount loaded at any instant increases beyond the value obtained for equilibrium pH 1.5. Hence, enhancement in the amount of metal extracted is totally attributed to the intensification caused due to the simultaneous extraction and stripping of zinc in ELM systems, stripping causes a revival of concentration gradient within the emulsion globules that results in a Zn flux within the emulsion.

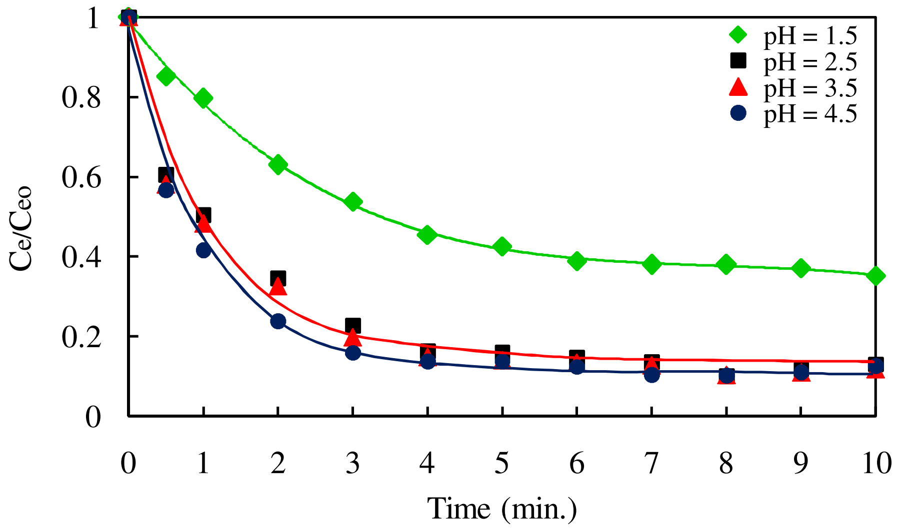


Fig. 5.2: Effect of pH on rate of zinc extraction
(ϕ=0.5, Cc=10% (v/v) D2EHPA, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6).

At pH 2.5 around 86% zinc recovery was obtained, while at pH 3.5 and 4.5 the extraction curves superimposed indicating that extraction rates were identical with maximum 90% recovery of zinc. The extraction rates at pH 3.5 and pH 4.5 were marginally larger than the rates obtained for pH 2.5.

An assessment was made of the pH drop during the course of the extraction based on initial feed pH=4.5 under actual operational conditions where Zn was being extracted by ELMs at two different sets of conditions that differed with respect to the amount of carrier present in the ELMs while all other factors remained identical. The results are shown in Fig. 5.3, where it is observed that initially there is a sharp decline in pH, subsequently the drop is only marginal.

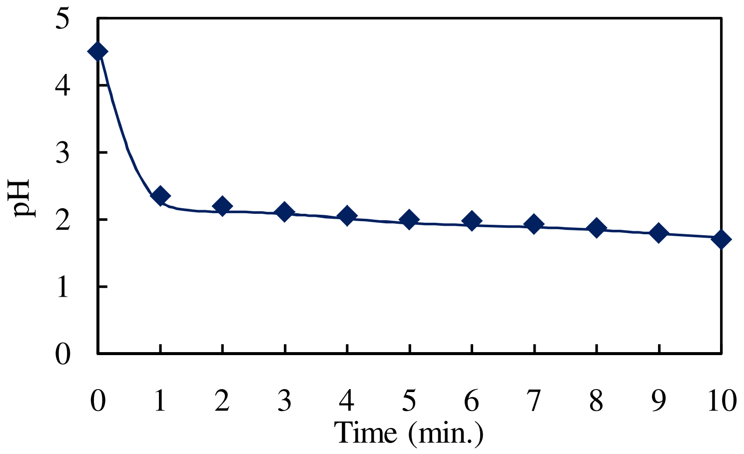


Fig. 5.3: Drop in feed phase pH during extraction of zinc under actual operating conditions

This behavior is attributed to minor breakage of the emulsion during dispersion; it could also be contributed to some extent by the internal acid phase adhering to the external surface of the emulsion. The sharp reduction in pH in the initial phase in a way masks out the other effect of gradual decline in pH due to release of proton etc. It also suggests that the actual extraction takes place under variable pH conditions in all cases at least during the initial phase of the experimental runs.

Effect of initial feed concentration (Ceo)

The initial feed concentrations were varied in the range of 500 mg/L to 3000 mg/L in four stages. The ELM specifications and other process conditions are listed in Table 5.1. When Ceo is low, most of the solute diffusing within the emulsion globule is stripped by the internal phase droplets that are situated in the peripheral regions of the emulsion globule. When Ceo increases, the peripheral droplets get rapidly exhausted, necessitating the solute to permeate deeper within the globule prior to get stripped. Therefore, an increase in Ceo also corresponds to an increase in diffusional path lengths. Increased path lengths lead to an decline in the rates of extraction as observed in Fig 5.4. There was no difference in the extraction rates between Ceo 500 mg/L and 1000 mg/L However, as the Ceo was increased to 2000 mg/L there was substantial decline in rates. The extent of extraction also declined from 90% to 77% in 10 minutes contact. Further increase in the feed concentration of zinc led to decline in the extent of extraction to 69%.

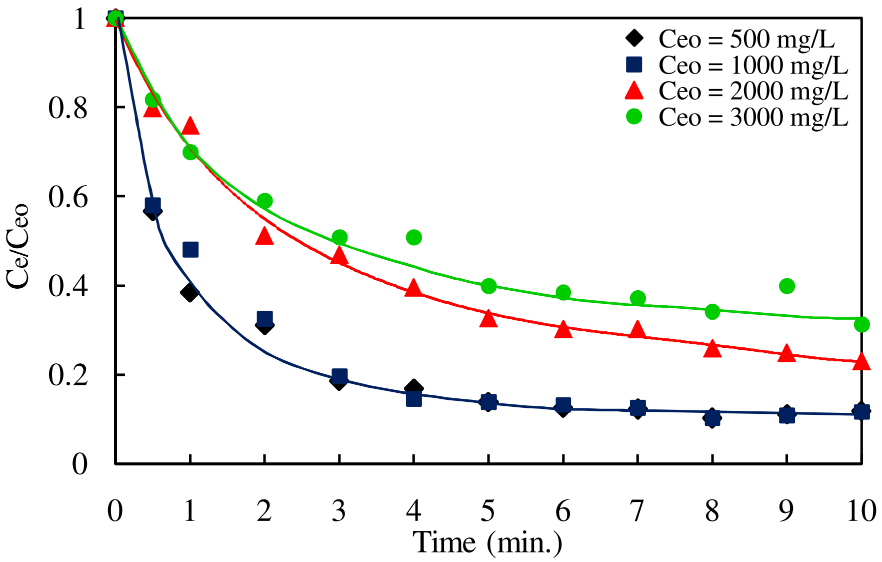


Fig. 5.4: Effect of initial feed concentration on rate of zinc extraction (pH=4.5, ϕ=0.5, Cc=10% (v/v) D2EHPA, Cio=1.5 M, TR=1:6)

Although from Fig. 5.4 it is seen that extraction rate for the case of Ceo (3000 mg/L) is considerably lower when compared with Ceo (500 mg/L), but in absolute terms of metal loaded such interpretations are subject to falsification, because at Ceo=500 mg/L, about 410 mg/L zinc was extracted from the feed in 10 min run duration while with Ceo=1000 mg/L the same amount gets loaded in just 0.8 min and with 2000 mg/L it gets loaded in 0.6 min. Thus increasing the initial feed concentration the rate of extraction also increases substantially while keeping all other conditions identical thereby establishing the kinetic dependence of the rates on the feed concentration.

Effect of treat ratio (TR)

Treat ratio (TR) is the ratio of the emulsion phase to the feed phase; it is a measure of the emulsion holdup in the system. Increase in treat ratio results in an increase in the extraction capacity of the emulsion. It also results in an increase in the amount of carrier and overall surface area for mass transfer in the system. An increase in treat ratio is expected to increase both the rate and extent of extraction.

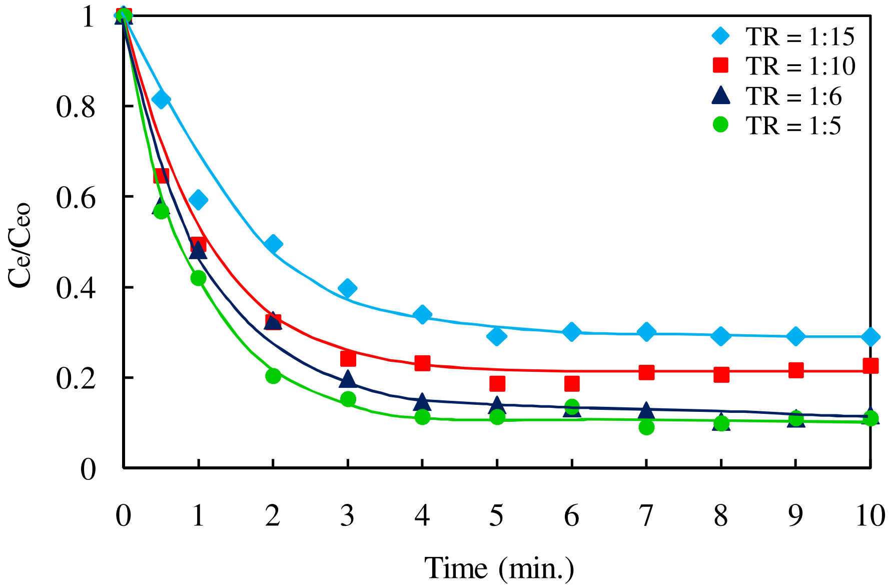


Fig. 5.5: Effect of treat ratio on rate of zinc extraction
(pH=4.5, ϕ=0.5, Cc=10% (v/v) D2EHPA, Cio=1.5 M, Ceo=1000 mg/L)

Fig. 5.5 shows the effect of treat ratio on extraction behavior for four cases. The ELM specifications and other process conditions are listed in Table 5.1. When the emulsion phase holdup was low, corresponding to TR (1:15), the rate of extraction was the least. Increasing emulsion holdup to TR (1:10 to 1:6) substantially increased the rate as well as the total extent of extraction but further increase in emulsion holdup to TR (1:5) did not substantially enhance the rates or the extent of zinc extraction.

Increase in emulsion holdup results in a plethora of complex effects, it increases the amount of extractant in the system and on the other hand results in formation of larger globules. It shifts the globule size distribution to the higher end of the spectrum. Larger globule sizes lead to a decrease in external mass transfer areas that in some cases become rate-limiting. Large globules also cause an increase the effective diffusion path lengths within the globule that results in a decline in extraction rates. Increase in emulsion hold-up also enhances globule – globule interactions causing globule breakage, globule coalescence, redispersion, etc., which result in release of the encapsulated zinc back to the feed phase. Hence, increase in treat ratio brings forward a net effect which is a complex interaction of all these effects and it is not easy to decipher any single cause as dominant. In this case, at least apparently it appears that increase in extractant concentration is the prime reason for the enhancement of extraction rates.

5.3.2 Effect of emulsion composition variables

Effect of internal phase volume fraction (ϕ)

The internal phase volume fraction of the emulsion has a profound influence on all properties of the emulsion. Increase in ϕ also enhances the capacity of the emulsion to extract the solute due to an increase in the stripping acid volume in the system. The major emulsion properties that change significantly due to an increase in ϕ are (i) emulsion viscosity, which makes the emulsion more difficult to disperse under identical conditions leading to formation of larger globules and (ii) increase in internal phase drop diameters when emulsions are formulated in the same manner as they were formulated for emulsions having lower ϕ, this reduces the mass transfer surface area. These two effects complement each other in reducing the rates of extraction. On the other hand increase in ϕ also causes a decline in the membrane volume that results in thinner membranes thereby reducing the diffusion path length within the emulsion globule thereby facilitating the rates but on the other hand it reduces the membrane fraction of the ELMs thus reducing the carrier content, which would have a detrimental influence on the rates of extraction.

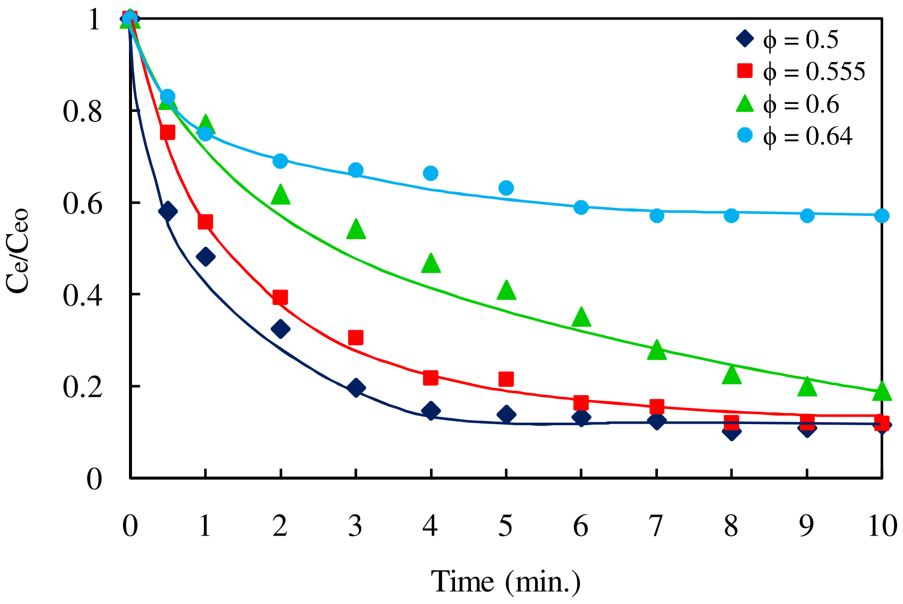


Fig. 5.6: Effect of internal phase volume fraction on rate of zinc extraction (pH=4.5, Cio=1.5 M, Cc=10% (v/v) D2EHPA, Ceo=1000 mg/L, TR=1:6)

Fig. 5.6 shows that, as ϕ is varied from 0.5 to 0.64 at a feed phase pH 4.5, keeping other process and emulsion parameters constant as shown in Table 5.1, there is a drastic decline in the rates of extraction. The difference in rates is not very prominent when ϕ changes from 0.5 to 0.555, but is substantial when ϕ increases from 0.555 to 0.60 and finally to 0.64. Table 5.2 below gives an idea of the wide variation in the viscosity and internal drop diameters of the emulsion with a change in ϕ.

Table 5.2 Variation in viscosity and internal drop diameter of the emulsion with change in internal phase volume fraction.

ϕ	Viscosity (cP) at 20 s^{-1}	Internal drop diameter (μm)
0.5	41.77	5.6507
0.555	86.61	6.3350
0.6	128.32	7.0366
0.64	189.8	7.6142

It was interesting to note that the final extent of extraction for ϕ values of 0.5, 0.555 and 0.60 were very close indicating almost 80% to 85% extraction of zinc but for ϕ values of 0.64 the extent of extraction reduced to 40%. The plausible reasons for this behavior is discussed earlier, it is however difficult to pin point any single factor causing this effect, it is very likely that this pattern arises due to ~ 28% decline in the carrier content that could be augmented by decline in pH from 4.5 due to emulsion breakage during dispersion.

Effect of internal phase acid concentration (Cio)

The capacity of the emulsion to extract solute is affected by the internal phase stripping acid concentration, as the acid concentration increases the emulsions capacity to extract also increases except for those cases where low acid strengths are favorable for stripping like in the case of nickel. The effect of internal phase stripping acid concentration on extraction of zinc is shown in Fig. 5.7 with emulsions having specifications mentioned in Table 5.1.

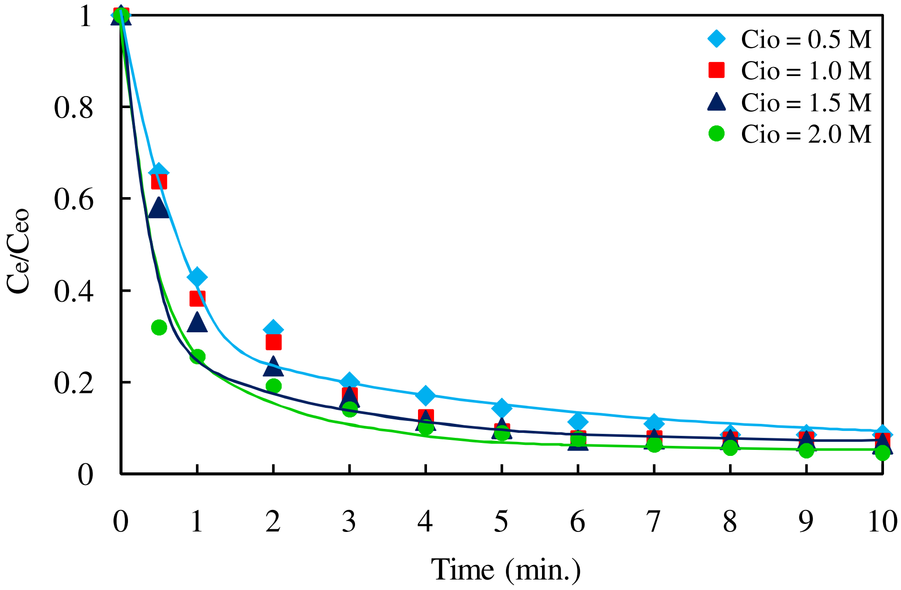


Fig. 5.7: Effect of internal phase acid concentration on rate of zinc extraction (pH=4.5, ϕ=0.5, Cc=10% (v/v) D2EHPA, Ceo=1000 mg/L, TR=1:6)

Fig. 5.7 shows that there is a no significant change in extraction rates with an increase in internal phase acid concentration from 0.5 M to 2.0 M. These extraction curves were obtained for otherwise identical operating conditions; the near convergence of extraction curves at 10 min duration indicates that the total extent of extraction was almost same for all four cases.

Effect of carrier concentration (Cc)

Carrier concentration plays a vital role in the overall extraction behavior of an ELM system. Fig. 5.8 shows the effect of carrier concentration on extraction behavior. Increase in the carrier concentration in the oil membrane phase of the emulsion from 2% (v/v) to 10% (v/v) leads to enhancement of zinc removal from feed phase. Increase in the carrier concentration in the range under investigation also augments the rate of extraction in another fashion, utilizing the surface active nature of the extractant. Decline in carrier concentration causes an increase in interfacial tension (γ) between the emulsion and feed phase, which leads to an increase in emulsion globule size thereby lowering the external surface area and as a consequence lowering the extraction rates as well.

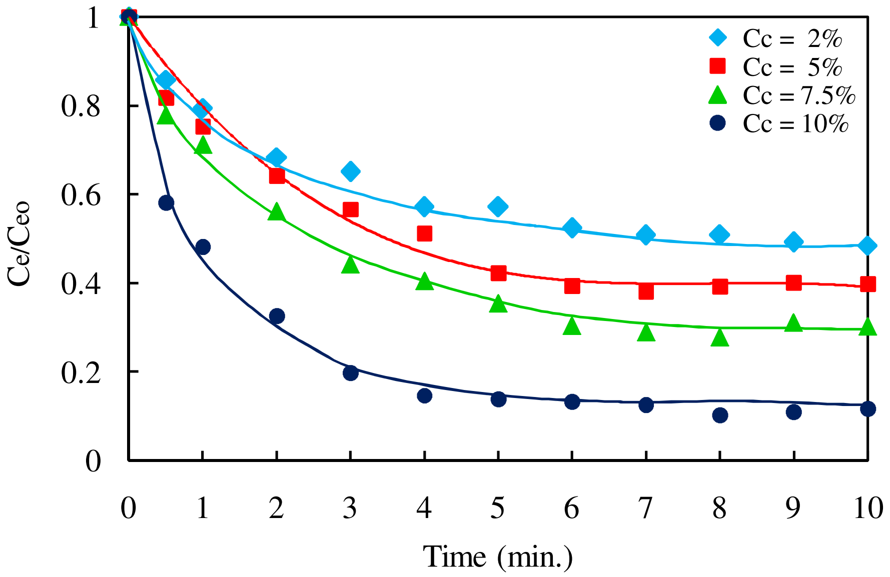


Fig. 5.8: Effect of carrier concentration on rate of zinc extraction using D2EHPA
(pH=4.5, ϕ=0.5, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

Some extractants have a tendency to aggregate at high concentrations that tends to reduce its metal binding capacity, consequently decline in extraction rates are observed at these carrier concentrations deviating from the usual trend of increase in extraction rates with increase in carrier concentrations as observed by Sengupta *et al.* (2006).

5.4 Zinc extraction using PC 88A into ELMs

PC 88A has been rarely used as a carrier in emulsion liquid membranes although it is very widely used in the solvent extraction of metals particularly for Co – Ni separations. The one instance when PC 88A was used in ELMs was to achieve selective cobalt recovery by Kasaini *et al.* (1998). PC 88A was used in supported liquid membranes to separate Zn from sulphate media containing zinc and cadmium by Juang *et al.* (2004). In this study effect of all the parameters that were investigated for zinc extraction using D2EHPA in previous section are also investigated using PC 88A as carrier.

5.4.1 Effect of process parameters

Effect of pH

It has already been observed that the pH of solution has a profound influence on the extraction rates of metals using ELMs. Extraction of Zn(II) from an 1000 mg/L aqueous sulphate solution was carried out using 10% (v/v) PC 88A at conditions listed in Table 5.1 using PC 88A as the carrier. The extraction rates of zinc in ELMs were determined at feed phase pH values of 1.5, 2.5, 3.5 and 4.5 as in the case of extraction using D2EHPA as the carrier. The extraction patterns are presented in Fig. 5.9.

The rate of zinc permeation in ELMs at pH 1.5 was found to be remarkably slow. Increasing the initial feed phase pH from 1.5 to 2.5, the extent of zinc removal at the end of the run increased phenomenally from 14% to ~ 80%. Further increase in pH from 2.5 to 3.5 did not show noticeable increase in the extent of extraction at the end of run but in the first half of the run the extraction rates were significantly faster. At pH=4.5 the rates of extraction were same as that observed for pH=3.5 and both the extraction curves get superimposed on each other.

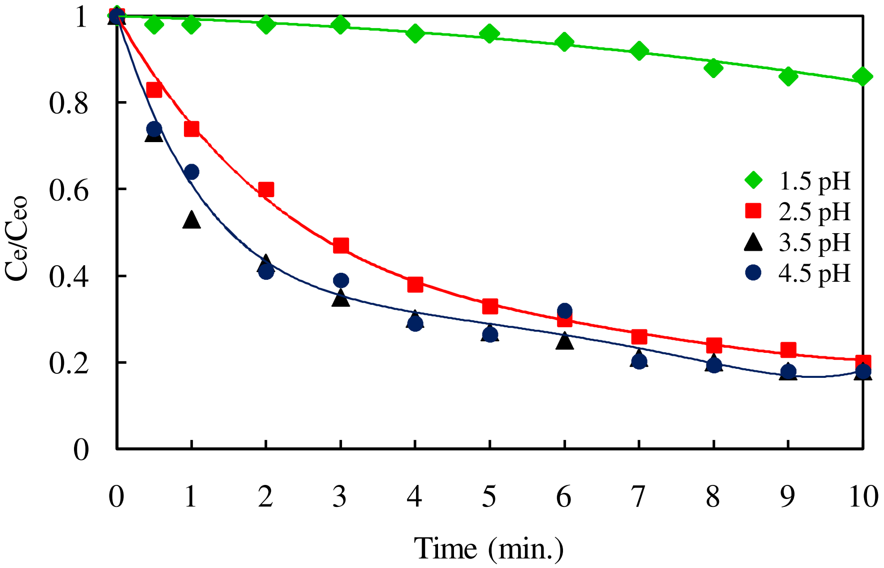


Fig. 5.9: Effect of pH on rate of zinc extraction
(ϕ=0.5, Cc=10% (v/v) PC 88A, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

The extraction pattern observed for ELMs in Fig. 5.9 is in consonance with the extraction isotherm shown in Fig 5.1. At equilibrium pH=1.5 the isotherm in Fig. 5.1 suggests initiation of the extraction with about 20% extraction, while pH=2.5 though located at the rising part of the isotherm accounts for almost 80% zinc extraction. Quantitative extraction is indicated at pH values of 3 and more hence, no difference in extraction profiles are observed for extraction at pH=3.5 and pH=4.5.

Effect of initial feed concentration (Ceo)

It is known that with increase in the initial feed solute concentration while maintaining all other parameters constant, the overall removal efficiency of ELMs decreases. This phenomenon results mainly due to the limitation in amounts of available carrier in the membrane phase and/or stripping agents in the internal phase. The influence of varying the initial concentration of zinc in the feed phase from 1000 mg/L to 3000 mg/L on the extraction rates of zinc are presented in Fig.5.10. The ELMs used were formulated using emulsion and operating variables listed in Table 5.1. It is observed that the degree of removal declines as the initial zinc content increases.

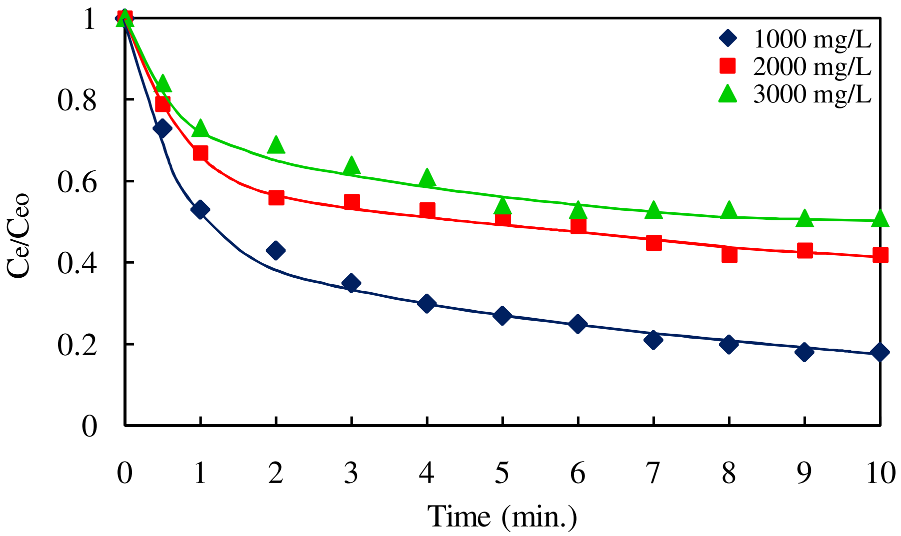


Fig. 5.10: Effect of initial feed concentration on rate of zinc extraction (pH=4.5, ϕ=0.5, Cc=10% (v/v) PC 88A, Cio=1.5 M, TR=1:6)

The main reason for the decline in extraction rates with an increase in initial feed concentration stems from two plausibility that are complimentary in reducing the rates. First plausibility is that the extractant capacity and concentration may be limiting the rates, i.e. the carrier binds with metal as per its capacity and then transports it to the inner droplets (internal interface) where the metal gets stripped. The free carrier returns back to the feed interface (external interface) to again bind with metal and transport them to the internal interface. This repeated shuttling of carrier between the external and internal interface enhances the diffusional path length traversed and thereby declines the overall rates of extraction. The second plausibility is that the carrier has large binding capacity and binds with the metal accordingly; this result in a large metal-carrier flux directed inside the emulsion globules. Due to the large influx of complex all the peripheral internal phase stripping droplets get depleted of their acid content quickly as a result the complex has to diffuse deep inside the globule to get stripped. This aspect also enhances the diffusion path length resulting in decline in the overall rates of extraction. However, if the second aspect is dominant then one should expect very rapid extraction in the initial phase of the run followed by a near plateau.

Effect of treat ratio (TR)

It is known that the volume ratio of the W/O emulsion to the feed solution controls interfacial mass transfer across ELMs. The influence of emulsion to external volume ratio in the range from TR=1:15 to TR=1:5, on the extraction of zinc is shown in Fig. 5.11 increasing ratio from 1:15 to 1:6 caused significant increase in zinc transfer rate and the capacity of the emulsion due to increase in the carrier content and interfacial area of contact at the external interface as well as in the inner interface of the ELMs.

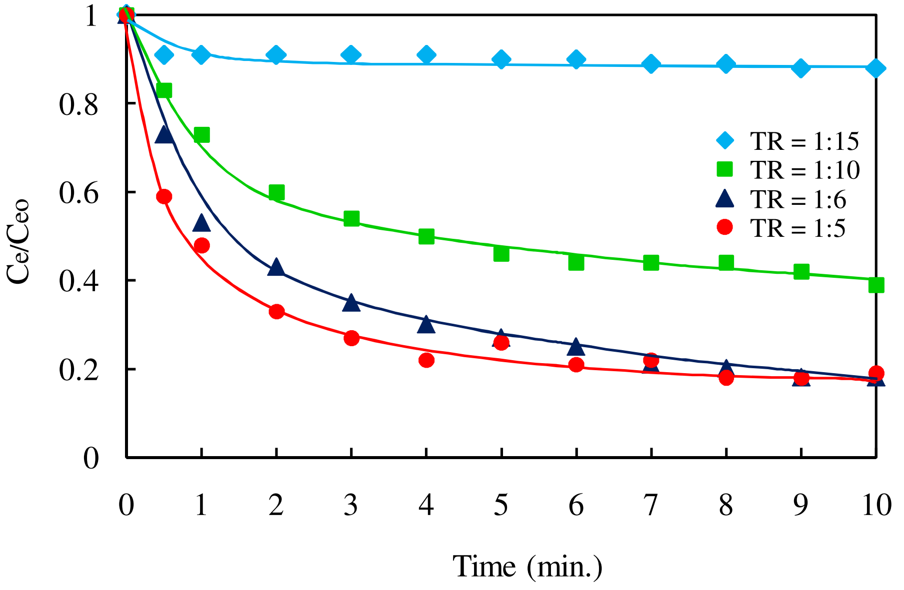


Fig. 5.11: Effect of treat ratio on rate of zinc extraction
(pH=4.5, ϕ=0.5, Cc=10% (v/v) PC 88A, Cio=1.5 M, Ceo=1000 mg/L)

Further increase in treat ratio from 1:6 to 1:5 enhanced the extraction rates at the initial part of the run but later the curves for treat ratio 1:5 and 1:6 merged after 8 minutes contact. Eventually the extent of zinc extracted in both cases was identical. Two factors appear to be contributing to this pattern of behavior, it is certain that increased treat ratio introduces more extractant as well as internal phase in the system, it also generates more surface area at least in the initial phase of the run due to dispersion of more amount of emulsion in the feed. Therefore, in the initial part of the run very rapid uptake of the metal is observed causing the driving force to deplete very rapidly thereby drastically reducing the rate of extraction as seen for TR=1:5 in Fig 5.11. The decline in rates are further augmented by factors like globule coalescence which is likely to be more pronounced in systems with greater emulsion hold up. When TR=1:5 the decline in driving force is more gradual and globule-globule interactions are at lower intensity hence extraction rates are more uniform throughout the run. The merger of plots is however purely coincidental, it only implies that for the given set of operating conditions and emulsion parameters TR=1:6 is optimal.

5.4.2 Effect of emulsion composition variables

Effect of internal phase volume fraction (ϕ)

It is known that the internal phase volume fraction of emulsion has a profound influence on its properties as a consequence the extraction behavior of ELMs also show wide variation when ELMs of varying ϕ are used. Increase in ϕ on one hand enhances the final capacity of the emulsion by increasing the stripping acid content but on the other hand it reduces the loading capacity of the emulsion by reducing the membrane fraction of the emulsion. Increase in ϕ reduces the diffusion path length within the globules but contributes to an increase in the size of globules.

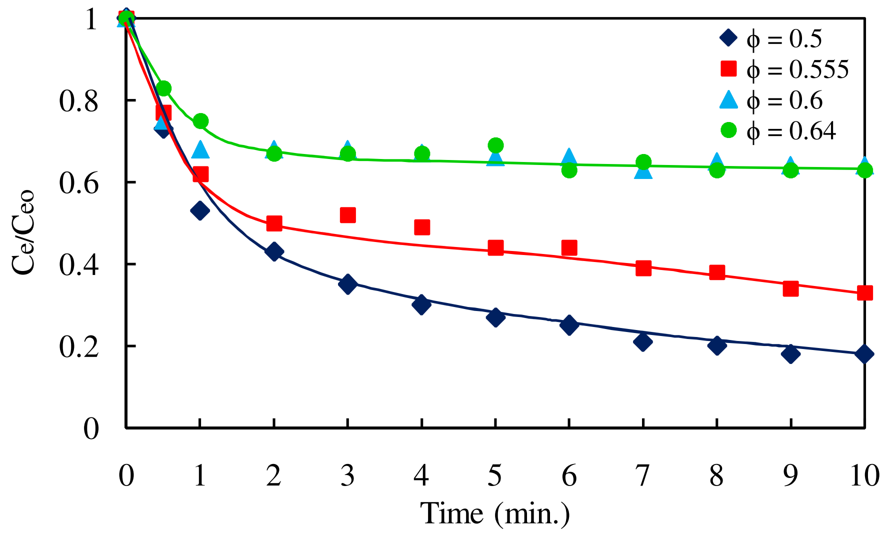


Fig. 5.12: Effect of internal phase volume fraction on rate of zinc extraction (pH=4.5, Cio=1.5 M, Cc=10% (v/v) PC 88A, Ceo=1000 mg/L, TR=1:6)

The extraction profiles for change in ϕ from 0.5 to 0.64 while maintaining all other parameters constant is shown in Fig 5.12. Increasing the internal phase volume fraction from 0.5 to 0.555 leads to an significant decline in rates accounting for ~ 15% less extraction from 4 minutes contact till the end of the run. Further increasing ϕ from 0.555 to 0.6 shows drastic reduction in rates with very little extraction taking place after two minutes of contact same is the case when ϕ is further increased to 0.64, only in the first minute of contact some distinction can be made in the extraction rates for ϕ values of 0.64 and 0.6 but for the rest of the run the amount extracted is almost the same Table 5.3 shows the extraction data observed for variation of ϕ up to two minutes of contact.

Table 5.3 Extraction data for variation of ϕ up to two minutes of contact.

Time (min.)	ϕ=0.5	ϕ=0.555	ϕ=0.6	ϕ=0.64
0	1	1	1	1
0.5	0.73	0.77	0.75	0.83
1	0.53	0.62	0.68	0.75
2	0.43	0.5	0.68	0.67

There is no doubt that increase in ϕ reduces the membrane phase content of the emulsion and proportionally the carrier content in the system because in all these runs carrier concentration was taken as 10% (v/v) of membrane phase but singularly this effect is not responsible for the decline of Zn uptake, because the net difference of carrier content in the system, between runs with ϕ=0.5 and ϕ=0.64 is 28% while the net amount extracted is ~ 45%. The decline in rates was also contributed by the rheological behavior of the emulsion. It was observed that the viscosity of the emulsion measured by cone and plate rheometer at shear rate of 20 s^{-1} at 25 ^{0}C was 33.17 cP for ϕ=0.5 and at identical conditions it was 269.04 cP for ϕ=0.64. This wide variation in viscosity changes the dispersion behavior at the prefixed dispersion speed of 150 rpm and causes the formation of large emulsion globules reducing the external surface area. This effect is further reinforced by corresponding increase in the internal droplet size on account of increase in the internal phase volume of the emulsion. The Sauter mean diameter calculated for internal droplet sizes was 5.424 and 6.653 micron for ϕ=0.5 and ϕ=0.64 respectively. Hence at larger values of ϕ the internal surface area also shows a corresponding decline due to increase in internal drop sizes.

Effect of internal phase acid concentration (Cio)

A series of experiments was carried out varying Cio in the range from 0.5 – 2.0 M to investigate the influence of internal phase sulfuric acid concentration on metal ion transfer. Fig. 5.13 shows the influence of the concentration of sulfuric acid as the internal stripping phase on the extent of zinc extraction.

It was found that the rates of extraction increased with increase in the concentration of sulfuric acid in the internal phase in the concentration range 0.5 to 1.5 M but with further increase in the acid concentration from 1.5 M to 2.0 M the rate of zinc extraction reduced.

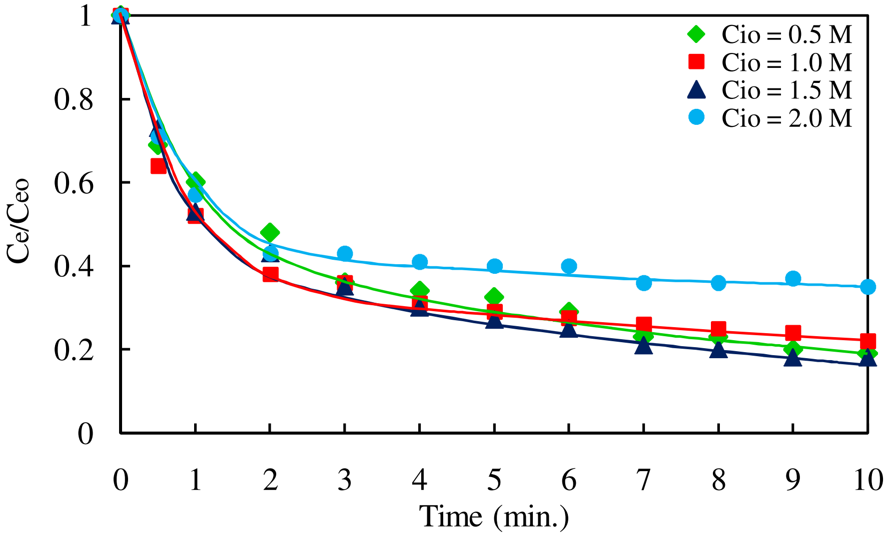


Fig. 5.13: Effect of internal phase acid concentration on rate of zinc extraction (pH=4.5, ϕ=0.5, Cc=10% (v/v) PC 88A, Ceo=1000 mg/L, TR=1:6)

The plausible reason for this behavior is the possibility of a pH swing taking place during initial dispersion of the emulsion caused by leakage of the internal phase of the emulsion in the feed phase. High acid concentration in the droplet phase also result in an increase in swelling due to large osmotic gradients between feed and internal phase, this also results in drop breakage.

Effect of carrier concentration (Cc)

Fig. 5.14 shows the effect of carrier concentration on the extraction rates, by increasing concentration of PC 88A from 2% (v/v) to 15% (v/v) the extraction of zinc was also increased almost dramatically. With 2% (v/v) PC 88A concentration around 20% extraction was recorded, increasing the carrier concentration to 5% (v/v) PC 88A results in an extraction profile that cannot be described as smooth, there is an oscillatory behavior in the data points that could arise because of shortage of carrier at the globule interface to bind with the metal. With an increase in carrier concentration to 10% (v/v), results in smooth and well defined extraction profile, it is interesting to note that as the carrier concentration increases from 2% (v/v) to 5% (v/v) the extent of zinc extracted almost doubles at given time intervals, further increasing carrier concentration from 5% (v/v) to 10% (v/v) again doubles the amount of zinc extracted at any given time interval this result indicates almost direct dependence of extraction rates on carrier concentration. This pattern happens only in two sets of conditions (1) When stripping is not taking place (2) Rate of stripping and extraction is identical. Further increasing PC 88A concentration to 15% (v/v) increases the rate and extent of extraction but its linear dependence on carrier concentration vanishes.

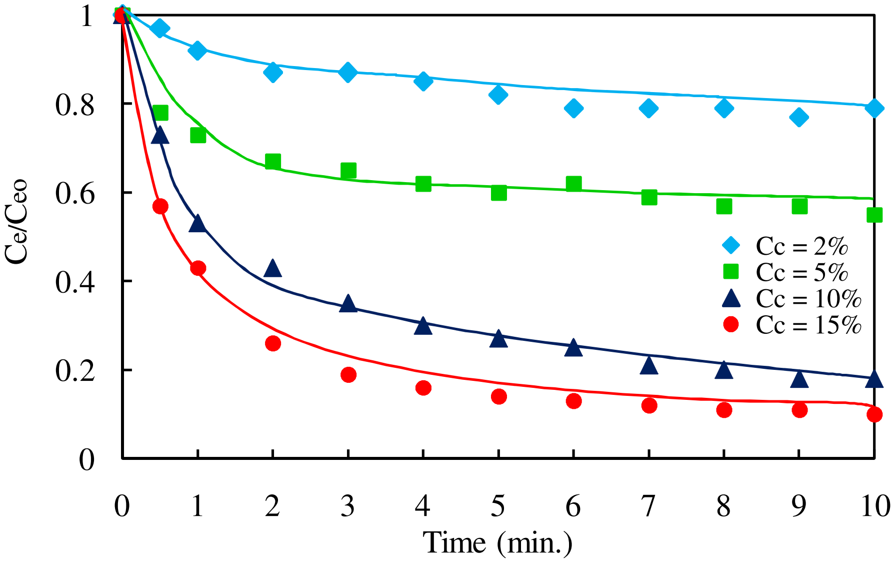


Fig. 5.14: Effect of carrier concentration on rate of zinc extraction using PC 88A (pH=4.5, ϕ=0.5, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

Since carrier is the most expensive agent among the other components of membrane, its lower concentration is always preferred. In all the experiments the concentration of PC 88A was maintained at 10% (v/v), unless otherwise stated.

5.5 Zinc extraction using CYANEX 302 into ELMs

CYANEX 302 has not yet been explored in ELMs as carrier although this extractant has been explored for solvent extraction studies with numerous cations. Mansur *et al.* (2008) have reported rather dismal performance of CYANEX 302 for zinc, iron and chromium extraction, the main problem encountered was the formation of a dense and viscous intermediate organic phase which they called *third phase*. Usually phase modifiers such as long chain alcohols are added to the solvent to avoid such third phase formation. In our solvent extraction experiments to determine pH isotherms, such problem was not encountered nor was any phase modifier added. However, it took more than usual time for separation of organic and aqueous phases post mixing. In experiments related to extraction using ELMs none of these difficulties surfaced. In the current investigation all the parametric variations investigated for D2EHPA and PC 88A as carrier in ELMs were also investigated for CYANEX 302 as carrier.

5.5.1 Effect of process parameters

Effect of pH

The extraction efficiency of zinc is affected by the acidity of the feed solution like other organophosphorous extractants.

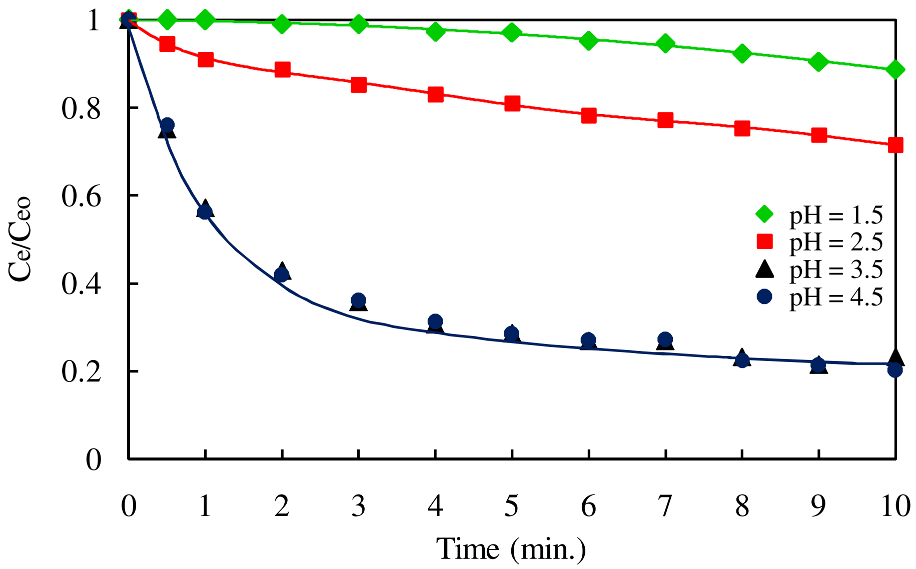


Fig. 5.15: Effect of pH on rate of zinc extraction
(ϕ=0.5, Cc=10% (v/v) CYANEX 302, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

As seen in Fig. 5.15 this effect is very pronounced at low pH values, only 10% of Zn extraction takes place at feed pH=1.5 which increases to 25% when pH is 2.5. The extraction efficiency increases with an increase of the feed pH up to a pH value of 3.5 any further increase of the pH does not alter the rate of extraction. These results corroborate with the pH isotherm plotted in Fig. 5.1 where quantitative extraction of zinc occurs using CYANEX 302 at pH=3.5 and above.

Effect of initial feed concentration (Ceo)

The initial concentration of zinc in the feed solution was varied 1000 – 3000 mg/L keeping all other parameters constant to evaluate the influence of Ceo on the rate of zinc transport in ELMs. The results are shown in Fig. 5.16, it is observed that at high initial feed concentrations although the percent removal is less but a large amount of zinc is transferred in the ELM phase. At Ceo=1000 mg/L the zinc removal is ~ 75% accounting for 750 mg/L removal, while at Ceo=3000 mg/L although the percentage zinc removal is only 40% but it accounts for 1200 mg/L in actual terms with the same amount and composition of emulsion phase in both cases.

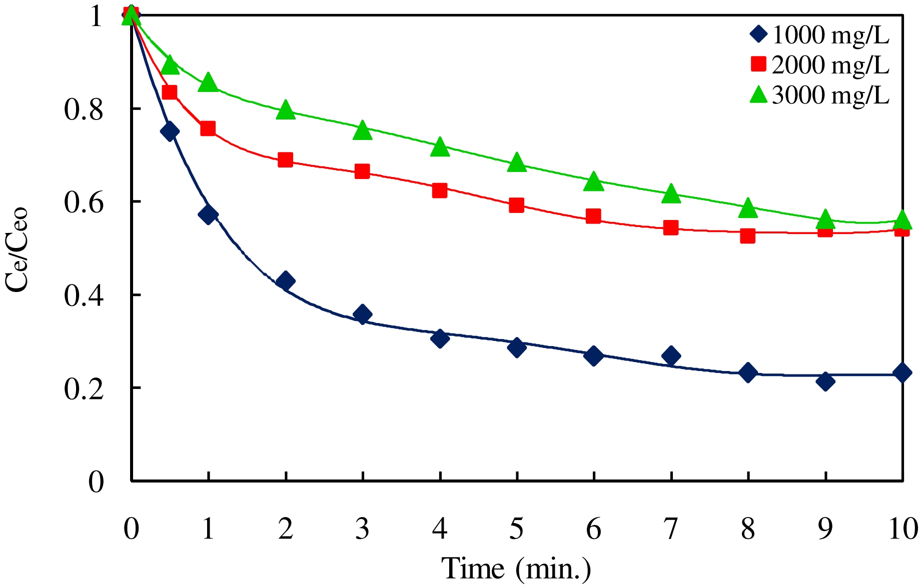


Fig. 5.16: Effect of initial feed concentration on rate of zinc extraction (pH=4.5, ϕ=0.5, Cc=10% (v/v) CYANEX 302, Cio=1.5 M, TR=1:6)

Effect of treat ratio (TR)

Increasing treat ratio always leads to an increase in extraction rates due to the increase in the extractant and strippant amount in the system as well as increase the surface areas. The experimental results are shown in Fig. 5.17. The extraction profile for TR 1:15 and 1:10 are nearly identical and superimpose of each other in these cases the amount of emulsion in the system was 40 ml and 60 ml and the strippant volumes were 20 ml and 30 ml respectively. The amount of metal extracted was only 60% of the initial feed concentration in both cases. Increasing treat ratios to 1:6 increased the rate and extent of extraction and almost 77% extraction was observed in 10 minutes duration.

Further increasing the treat ratio to 1:5 led to enhancement in the rates in the second half of the run although in the first 2 - 3 minutes the extraction rates were nearly identical. The final extent of Zn removal was ~ 82%. The difference observed in the extraction rates in these runs primarily stem from the increase in the membrane content in the system when TR=1:5.

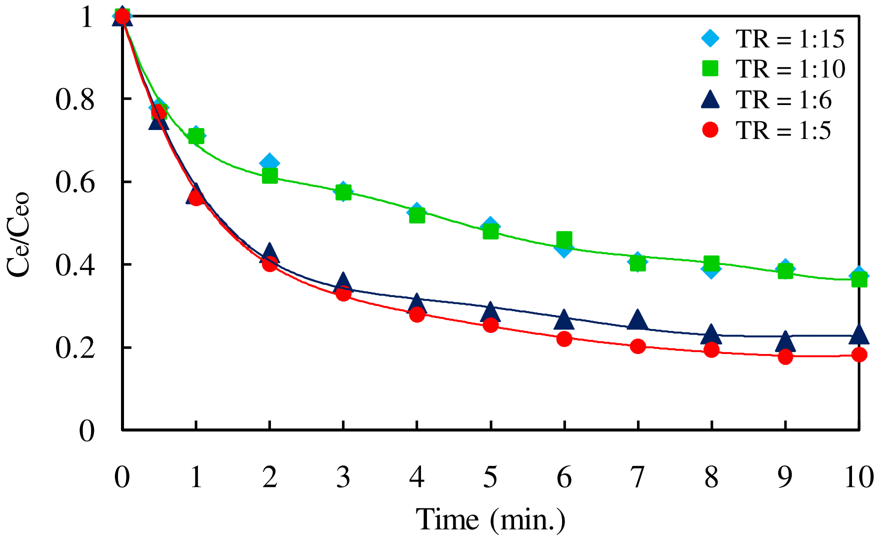


Fig. 5.17: Effect of treat ratio on rate of zinc extraction
(pH=4.5, ϕ=0.5, Cc=10% (v/v) CYANEX 302, Cio=1.5 M, Ceo=1000 mg/L)

Increased membrane phase content increases the carrier content in the system that helps in loading more Zn in the ELMs, it is unlikely that stripping of Zn plays any significant role in this process because it is known that stripping of Zn from CYANEX 302 – Zn complex is a slow process (Raghuraman *et al.* 1994).

5.5.2 Effect of emulsion composition variables

Effect of internal phase volume fraction (ϕ)

The effect of ϕ on the rates of extraction is shown in Fig. 5.18 the decline in extraction rates when ϕ increases from 0.5 to 0.555 is understandable on account of decrease of extractant content in the system and corresponding decrease in the external and internal surface areas. However, there was a drastic decline in rates observed when ϕ further increased from 0.555 to 0.6 accounting for ~ 50% decline in the total extent of Zn extraction. This pattern is unexplainable, because the decline in carrier concentration is ~ 20% between ϕ value of 0.5 and 0.6, the viscosity of emulsion at shear rate of 20 s^{-1} for ϕ=0.5 was 25.8 cP and for ϕ=0.64 it was 228.5 cP. Although there was almost a tenfold increase in viscosity, that would contribute to larger globule sizes but it does not justify the drastic decline in extraction rates for ϕ=0.6 and 0.64, moreover with D2EHPA as the carrier almost identical rheological behavior of the emulsion was observed at these ϕ values but the extraction rates did not portray such drastic changes between $0.55 < \phi < 0.6$.

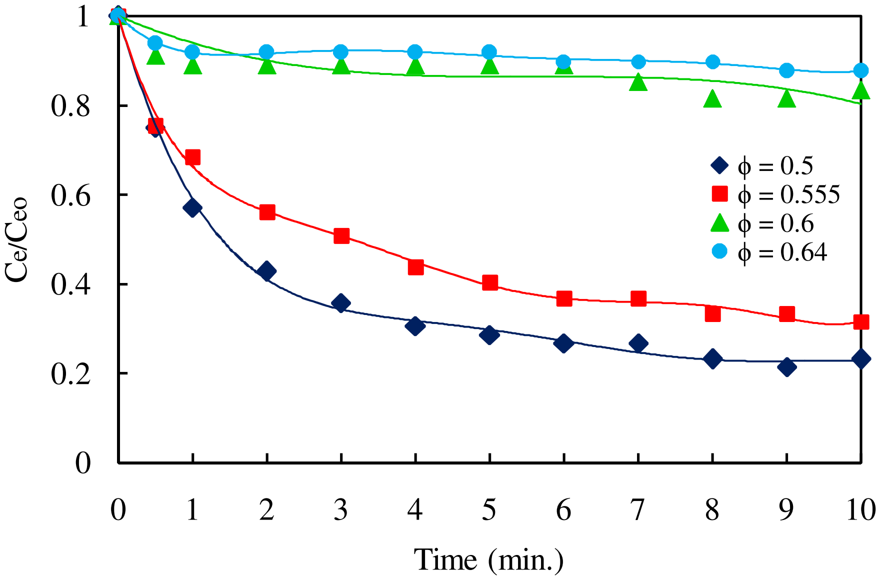


Fig. 5.18: Effect of internal phase volume fraction on rate of zinc extraction (pH=4.5, Cc=10% (v/v) CYANEX 302, Cio=1.5 M, Ceo=1000 mg/L TR=1:6)

There can be a number of reasons for such behavior (i) emulsion breakage during dispersion causing a pH swing, (ii) Very slow stripping rates that get slower at higher values of ϕ due to increase of internal droplet sizes that brings about a decline in the surface areas, (iii) presence of a surface active impurity that occupies the mass transfer surfaces inhibiting extraction and stripping. A more detailed investigation is required to address these issues.

Effect of internal phase acid concentration (Cio)

The stripping reaction at the internal interface plays a vital role in the transfer of metal ion from membrane side to internal phase droplets in an ELM process. The effect of stripping acid concentrations on the rate of Zn extraction using CYANEX 302 as carrier was investigated at different concentrations of sulfuric acid ranging from Cio=0.5 M to Cio=2.0 M, all other parameters such as pH of feed at 4.5, CYANEX 302 concentration in membrane phase at 10% (v/v), initial feed concentration at 1000 mg/L were kept constant. Fig. 5.19 shows the plot of Ce/Ceo against time for different stripping acid concentrations. It is seen that rate of extraction increases with increase in striping acid concentration from Cio=0.5 M to Cio=1.0 M. Further increase of acid concentration from 1.0 M to 1.5 M to 2.0 M did not increase the extraction rates particularly in the latter half of the run.

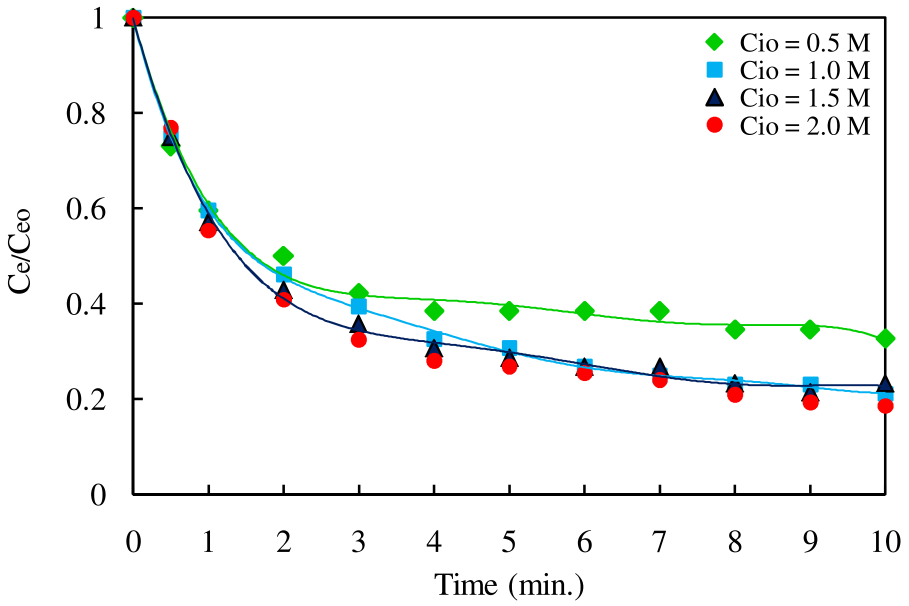


Fig. 5.19: Effect of internal phase acid concentration on rate of zinc extraction (pH=4.5, ϕ=0.5, Cc=10% (v/v) CYANEX 302, Ceo=1000 mg/L, TR=1:6)

The percentage of extraction at the end of the run varies from 68% to 79% as strip acid concentration increases from 0.5 M to 1.0 M. These results indicate that beyond a threshold concentration of stripping media (in this case 1.0 M) the rates do not get affected by strip acid concentration, it also implies that Zn complex with CYANEX 302 is strong and striping Zn from the complex is a slow process.

It is rather disappointing that the emulsions formed with CYANEX 302 with sulfuric acid in inner phase tend to be very stable and do not disintegrate easily; otherwise deeper insight of the striping behavior could have been drawn by analyzing the internal phase of the emulsion.

Effect of carrier concentration (Cc)

The effect of CYANEX 302 concentration in the membrane phase of the emulsion on zinc extraction from a feed containing 1000 mg/L was studied in the range 5% – 15 % (v/v). The pH of the feed solution was 4.5 and Cio was 1.5 M. Fig. 5.20 shows that as CYANEX 302 concentration increased from 5% to 15%, the extraction rate increased steadily, and the extent of extraction at the end of the run was 66%, 77% and 83% of zinc removed for 5%, 10%, 15% of carrier respectively.

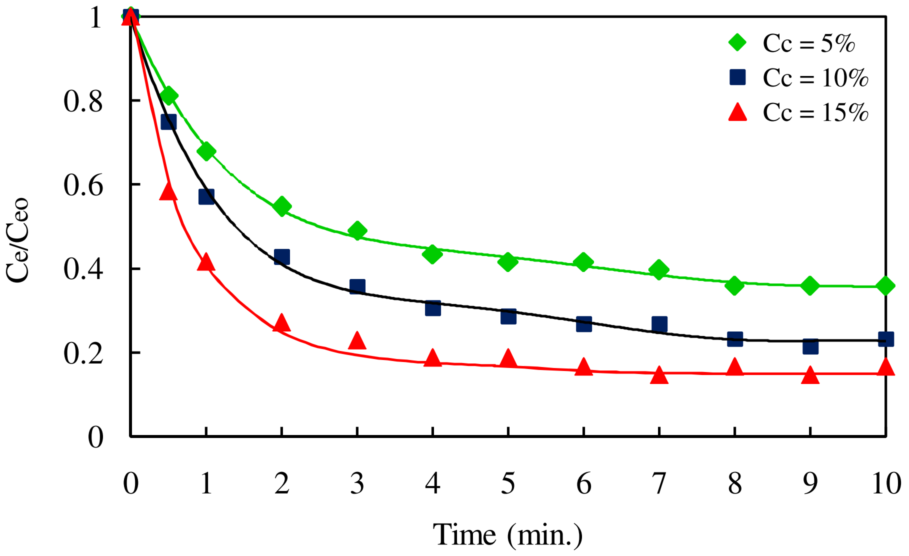


Fig. 5.20: Effect of carrier concentration on rate of zinc extraction using CYANEX 302 (pH=4.5, ϕ=0.5, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

5.6 Comparison of organophosphorous extractants for zinc extraction

While attempting a comparison of the observed extraction patterns of the three organophosphorous extractant D2EHPA, PC 88A and CYANEX 302 it needs to be noted that D2EHPA is somewhat like an universal extractant for metal ions. It has far wider range of application than the other two extractants but it is not selective, commercially it is most extensively used. In contrast to D2EHPA the other two extractants have narrow range of application and are targeted towards specific applications such as Co - Ni separation, separation of rare earths, cadmium separation etc where they function more selectively than D2EHPA.

Using these extractants as carrier in ELMs the effect of parametric variation on the rates of extraction with each extractant has been explored in the earlier sections. In this section the performance of the three extractants are compared in the parameter space to assess that region of parameter space where the behavior of individual extractants are most convergent.

Effect of feed pH

The pH of the aqueous feed phase is perhaps the most dominant parameter influencing the extraction behavior of zinc and other transition metal ions using organophosphorous reagents. A reagent that extracts metal species at lower pH has the advantage of operating over a wider range. The organophosphorous extractants D2EHPA, PC 88A and CYANEX 302 were used as carriers for the extraction of zinc from aqueous sulphate solutions into emulsion liquid membranes. The acidity of these three carriers is in the order D2EHPA > PC 88A > CYANEX 302, the pH_{50} (pH value at which 50% zinc is extracted from the feed) turns out to be 1.45, 1,83 and 2.14 for D2EHPA, PC 88A and CYANEX 302 respectively as seen from Fig. 5.1. Therefore, zinc gets extracted with D2EHPA at relatively lower pH values, it has been reported that D2EHPA is a good extractant for zinc in the pH range 1.5 – 3.

In ELM systems, since extraction and stripping takes place simultaneously, it is sometimes difficult to assess the effect of process parameters with a clarity equivalent to conventional solvent extraction. Still we find that under otherwise identical conditions the effect of pH is very clearly distinguishable with respect to the three organophosphorous extractants used as carriers. It is seen from Fig. 5.21 that at pH 1.5, D2EHPA extracts almost 60% of zinc in feed in 10 minutes while PC 88A and CYANEX 302 extract only about 12% that is in agreement with the extraction profiles shown in Fig. 5.1.

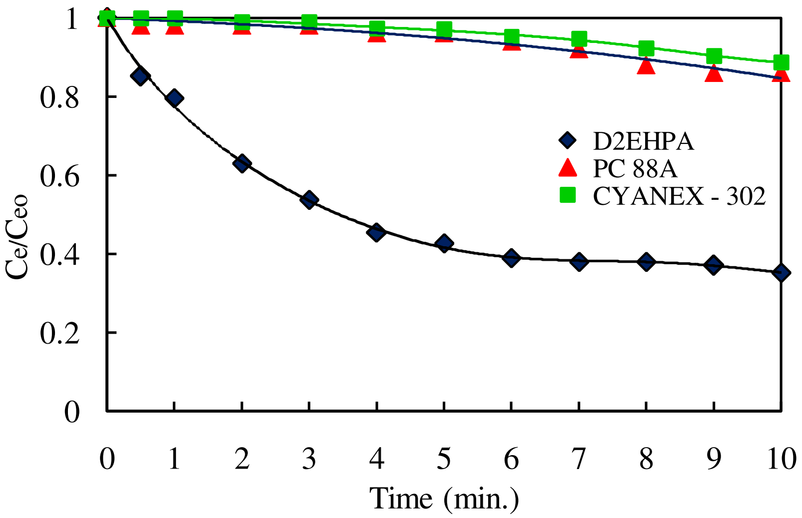


Fig. 5.21: Extraction of zinc using organophosphorous extractants at pH=1.5 (ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

At pH 2.5 the extraction curves for all the three extractants spread out as shown in Fig 5.22, the extent of extraction observed in 10 minutes time closely approximates the extraction profile shown in Fig. 5.1 for the extractants D2EHPA and PC 88A, however it trails short with CYANEX 302 possibly indicating the slow rate of zinc extraction using CYANEX 302. At pH 3.5 the pH isotherm in Fig. 5.1 shows quantitative zinc extraction with the three organophosphorous extractants investigated, but the extraction profile in ELMs does not reflect this behavior.

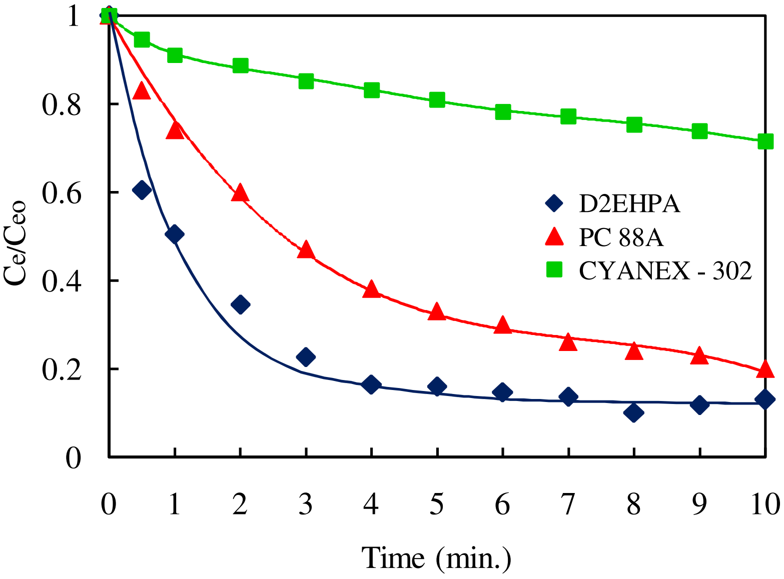


Fig. 5.22: Extraction of zinc using organophosphorous extractants at pH=2.5 (ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

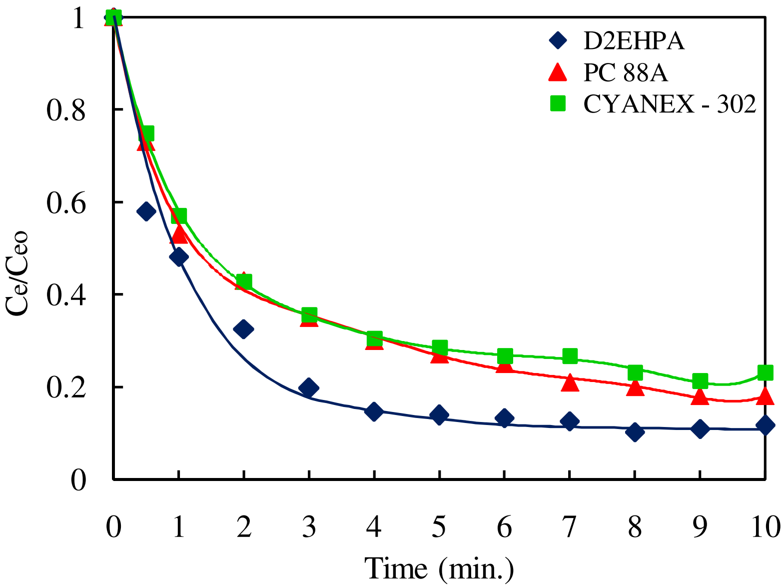


Fig. 5.23: Extraction of zinc using organophosphorous extractants at pH=3.5 (ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L, TR=1:6)

It is observed that D2EHPA extracts ~ 85% of the initial zinc in feed and gets saturated, while the other two settle for ~ 80% extraction of zinc. Once again we find PC 88A and CYANEX 302 extraction profile converging together but this time at the lower end of the figure in the higher extraction region. The different patterns of extraction observed at pH 3.5 primarily stem from the individual physicochemical traits of these extractants in the ELM system that effects emulsion properties as well as the stripping behavior of the metal complexes.

Effect of initial feed concentration (Ceo)

ELMs have shown a great potential for metal recovery from waste streams and run of mine waters where solute concentrations are relatively low and other techniques become expensive as well as inconvenient. Changing the solute concentration affects concentration driving force and possibly the mass transfer rates. The efficacy of D2EHPA, PC 88A and CYANEX 302 as carrier having concentration of 10% (v/v) was investigated at pH 4.5, and for varying concentration of zinc in feed solutions while keeping all other parameters identical The extraction profile of zinc with the three extractants is shown in Fig. 5.24 and Fig. 5.25.

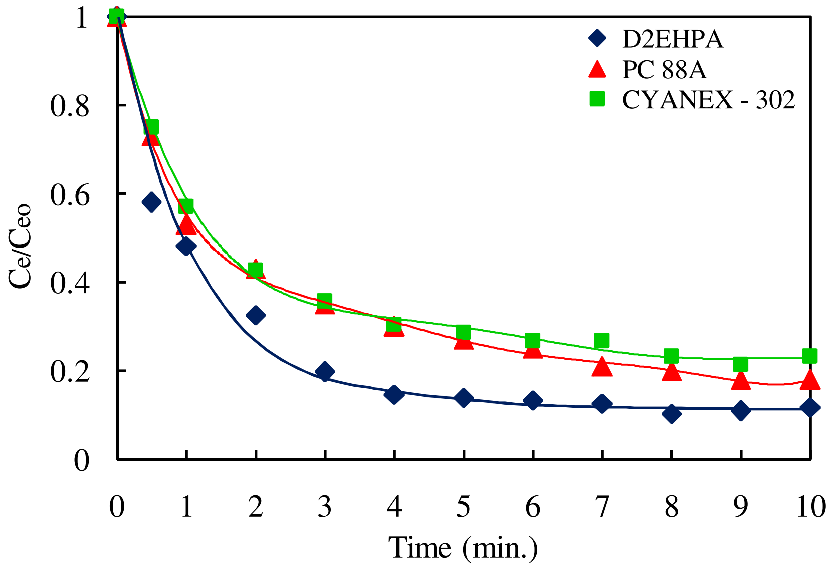


Fig. 5.24: Extraction of zinc using organophosphorous extractants at Ceo=1000 mg/L (pH=4.5, ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, TR=1:6)

The extent of extraction based on initial feed concentration shows a decline with an increase in the initial feed concentration although the net amount extracted by the ELMs increase substantially when feed concentration is high, for example PC 88A extracts 80% of initial zinc when the feed concentration is 1000 mg/L but only ~ 45% when the feed concentration is 3000 mg/L this however translates to 800 mg of Zn removed in the first case and 1350 mg in the second case per liter of feed processed.

It is reasonable to expect a decline in the rate of extraction of zinc by ELMs, when the amount of carrier in the membrane phase is constant, with an increase in feed concentration. The large inward flux of the metal complex depletes the stripping agent from the internal droplets of the emulsion in the peripheral region forcing the zinc complex to diffuse deeper in the globule through the membrane phase to encounter the internal droplets to get stripped. This results in longer diffusion path lengths causing the rates to decline.

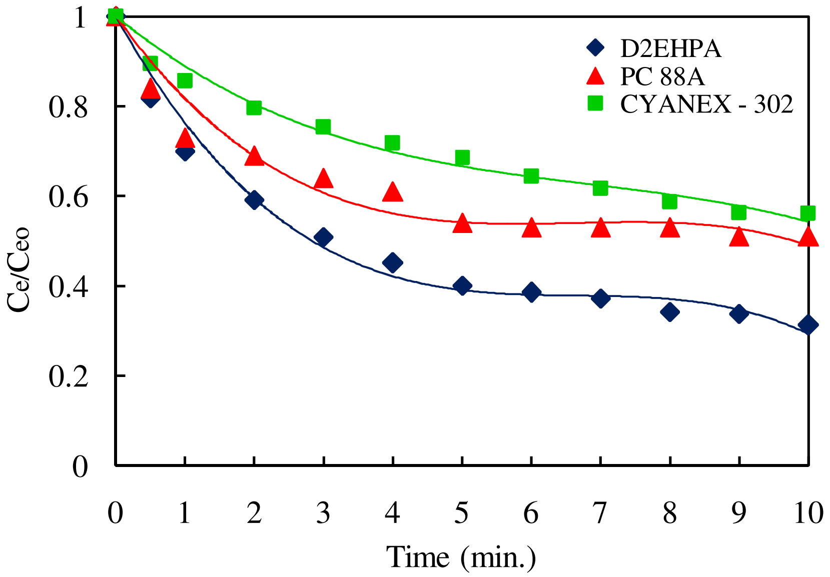


Fig. 5.25: Extraction of zinc using organophosphorous extractants at Ceo=3000 mg/L (pH=4.5, ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, TR=1:6)

Comparing the extractants one finds that the difference in rates become more pronounced at feed concentrations of 3000 mg/L in comparison to 1000 mg/L which can be attributed to the difference in diffusion coefficients of these extractants in kerosene and the kinetics of loading and stripping of zinc from these extractants.

Effect of treat ratio (TR)

The treat ratio it is a measure of the emulsion holdup in the system, increasing the treat ratio results in an increase in the capacity of the emulsion for extraction of solutes. Increase in treat ratio increases the loading capacity of the emulsion by increasing the membrane phase and the carrier content in the system, it increases the storing capacity by increasing the internal phase and it increases the mass transfer area by increasing the number of emulsion globules formed on dispersion of the emulsion in the feed.

The treat ratio was varied by changing the amount of emulsion added to the feed phase in the range 1:15 to 1:5 keeping all other parameters constant.

Comparing the performance of the three extractants it is seen that with D2EHPA there is only marginal enhancement in the amount extracted from ~ 65 to 85% on changing treat ratio from

1:15 to 1:6 i.e. increasing the amount of emulsion from 40 ml to 100ml in 600 ml feed. Among the extractants PC 88A is most sensitive to TR, when TR is 1:15 only 10% extraction is recorded that increases to 60% and 80% for TR of 1:10 and 1:6 respectively.

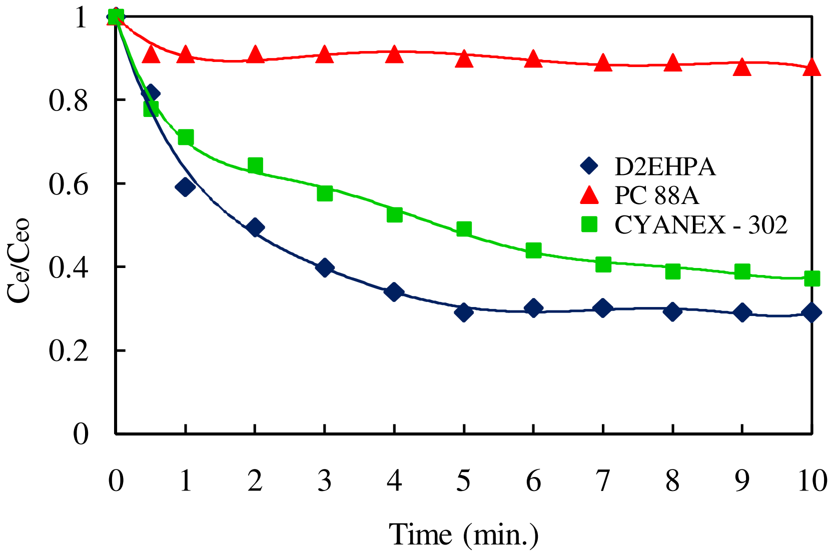


Fig. 5.26: Extraction of zinc using organophosphorous extractants at TR=1:15 (pH=4.5, ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L).

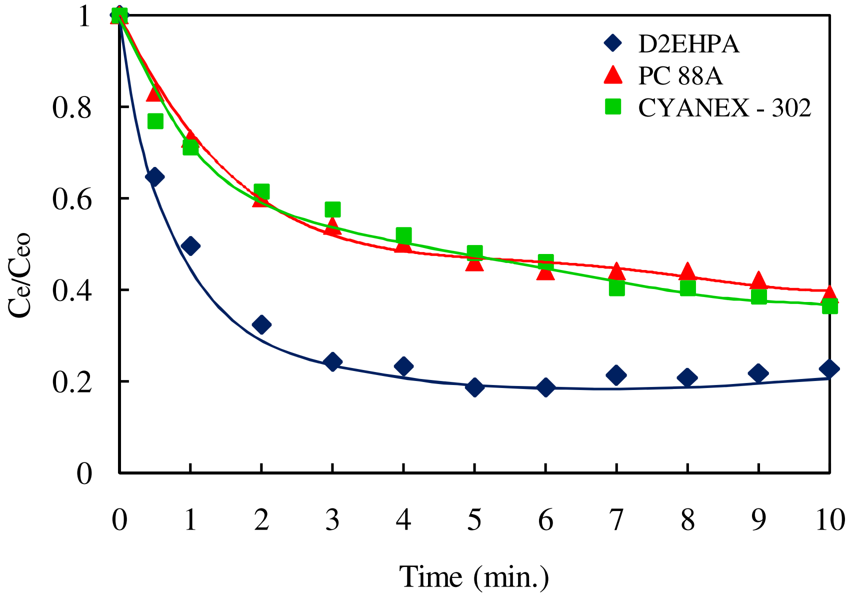


Fig. 5.27: Extraction of zinc using organophosphorous extractants at TR=1:10 (pH=4.5, ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L).

On the other hand CYANEX 302 is highly insensitive to treat ratio it records ~ 60% zinc removal at TR 1:15 and 1:10 that increases to 75% at TR of 1:6. A plausible explanation to this behavior needs greater insight in the loading and stripping behavior of these extractants and needs to be explored further.

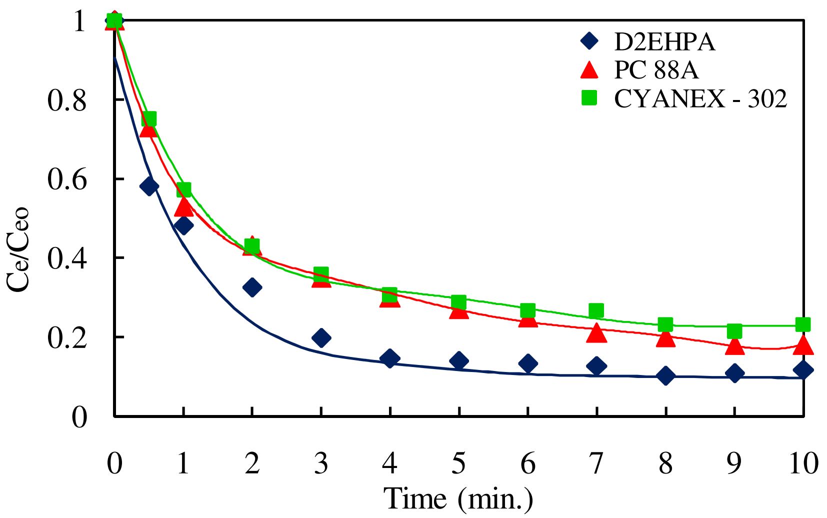


Fig. 5.28: Extraction of zinc using organophosphorous extractants at TR=1:6 (pH=4.5, ϕ=0.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L).

Effect of internal phase volume fraction (ϕ)

Increase in the internal phase volume fraction of the emulsion changes all measurable properties of the emulsion, it makes the emulsion very viscous hence difficult to disperse, it also reduces the extractant content in the system while increasing the storage capacity of the emulsion. The sensitivity and efficacy of the three extractants to an increase in ϕ while maintaining all other parameters constant are shown in Fig. 5.29 and Fig. 5.30

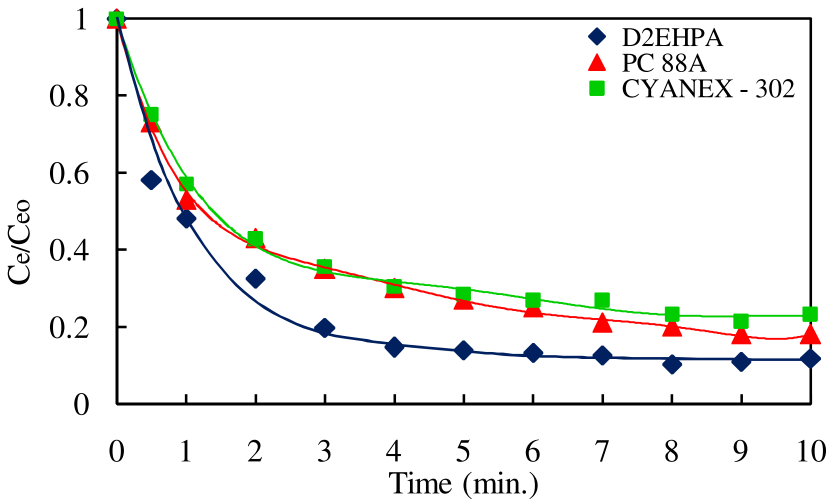


Fig. 5.29: Extraction of zinc using organophosphorous extractants at ϕ=0.5 (pH=4.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L, TR=1:6).

It is seen that an increase in ϕ from 0.5 to 0.6 in ELMs containing D2EHPA the results are distinctly different from the other two organophosphorous extractants. In ELMs containing

D2EHPA increase in ϕ slows down the extraction process that could be caused by (1) Reduction of carrier content by 20%, (2) Formation of larger globules because of increased viscosity causing a decline in surface area and corresponding increase in diffusion path lengths.

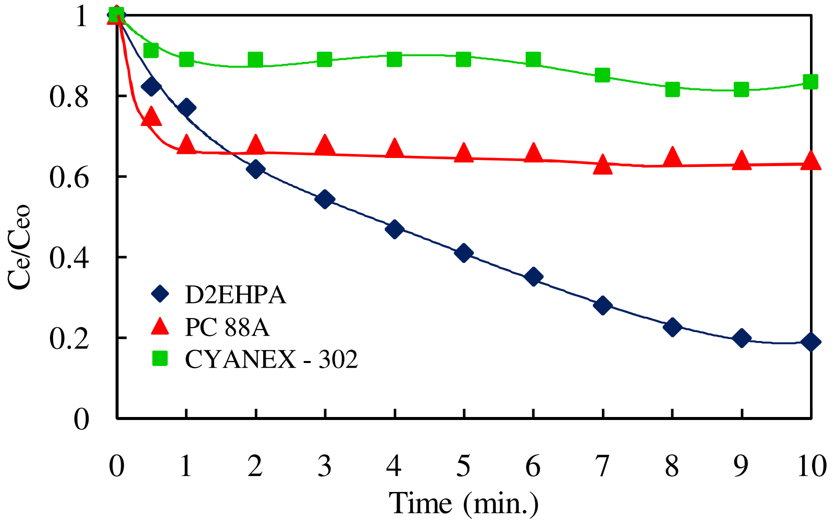


Fig. 5.30: Extraction of zinc using organophosphorous extractants at ϕ=0.6 (pH=4.5, Cc=10% (v/v), Cio=1.5 M, Ceo=1000 mg/L, TR=1:6).

In ELMs with PC 88A and CYANEX 302 increase in ϕ from 0.5 to 0.6 almost arrests the extraction after one minute of contact. Such behavior is not expected from the decline in extractant content in the system; it is likely to have been caused by leakage of internal phase of the emulsion in the feed during emulsion dispersion causing a fall in the pH that shifts the extraction equilibrium unfavorably.

Effect of internal phase acid concentration (Cio)

Since stripping process is an integral part of the ELM systems therefore, it is necessary to investigate the influence of stripping phase composition to obtain maximum rate of extraction of metal solutes using ELM techniques.

As the extraction step occurs in the interface between the feed solution and the liquid membrane, the metal ions necessarily requires a simultaneous back-extraction step (stripping) at the inner end of the membrane where the extractant is regenerated and the metal is stripped. The effect of stripping on the extraction process is determined indirectly by varying acid strength in the internal phase of the emulsion while keeping all other parameters constant. In the present study, a series of experiments was carried out with acid strengths ranging from 0.5

– 2.0 M to investigate the influence of internal sulfuric acid concentration on the overall zinc transfer in the ELM systems using the three extractants, results for stripping with 0.5 M and 2.0 M is shown in Fig. 5.31 and Fig. 5.32.

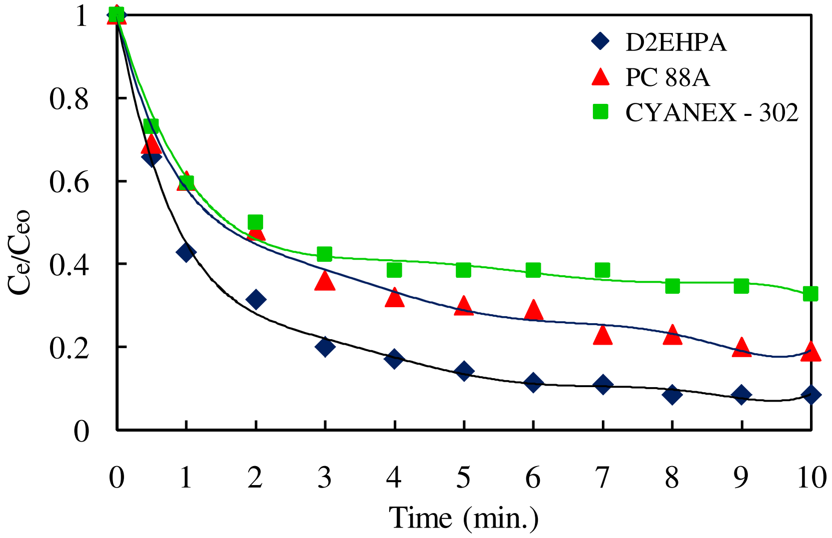


Fig. 5.31: Extraction of zinc using organophosphorous extractants at Cio=0.5 M (pH=4.5, ϕ=0.5, Cc=10% (v/v), Ceo=1000 mg/L, TR=1:6).

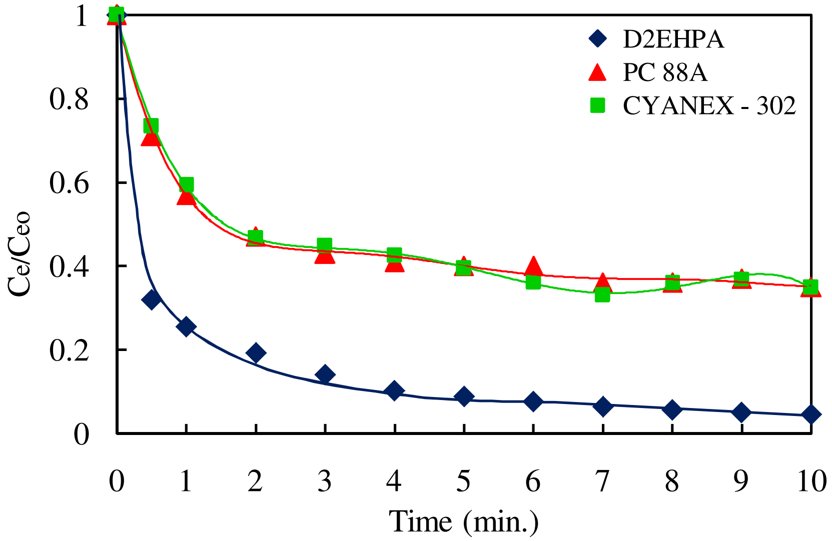


Fig. 5.32: Extraction of zinc using organophosphorous extractants at Cio=2.0 M (pH=4.5, ϕ=0.5, Cc=10% (v/v), Ceo=1000 mg/L, TR=1:6).

It is seen that the amount of zinc loaded in emulsions with D2EHPA as carrier was not very sensitive to acid concentration, the other two extractants also did not show prominent effect of stripping acid concentration. It is likely that the actual effect is masked by other factors that aid or marr the stripping rates such as the internal surface area of the emulsion which is so large that even at very slow rates of stripping sufficient amount of the metal could get stripped. One effect however stands out particularly observed with Cio=2.0 M is the decline of extraction using PC 88A and CYANEX 302 that results because of the leakage of internal phase during dispersion causing a pH swing. This effect is however not observed with D2EHPA that has the capacity to extract zinc from highly acidic solutions on account of it low pK_a values.

Effect of carrier concentration (Cc)

The concentration of all three extractants was varied in the range from 5% – 15% v/v to determine the effect of the carrier concentration on the extraction of zinc. D2EHPA concentration did not seem to affect the extraction rate for zinc significantly in the range of 2% to 10%. The interfacial tension sharply decreased with increasing D2EHPA concentration that result in formation of smaller globules at higher D2EHPA concentrations.

At 5% (v/v) carrier concentration D2EHPA and CYANEX 302 show nearly similar extraction profile as can be seen from Fig. 5.33 and Fig. 5.34, while at 10% carrier concentration PC 88A and CYANEX 302 show nearly similar extraction profiles.

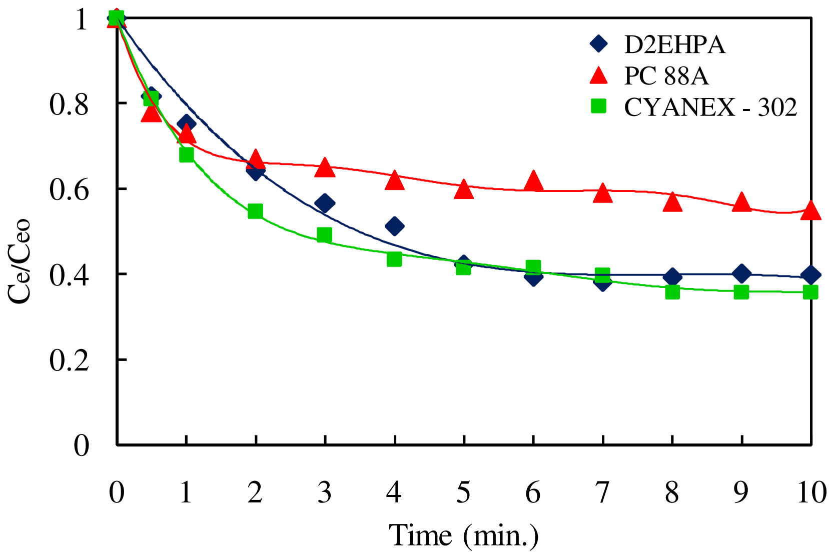


Fig. 5.33: Extraction of zinc using organophosphorous extractants at Cc=5% (v/v) (pH=4.5, ϕ=0.5, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6).

The behavior of PC 88A at 5% concentration seems quite ill defined because initially the extraction rates are high but later it declines. This trend was not seen with the other extractants. Increasing the carrier concentration to 10% eliminated this jerky behavior.

Increasing carrier concentration to 15% did not enhance the rates of extraction significantly for the three extractants. The results unambiguously indicated that 10% carrier concentration in the membrane phase is the optimal amount of organophosphorous extractant to be incorporated in an ELM system.

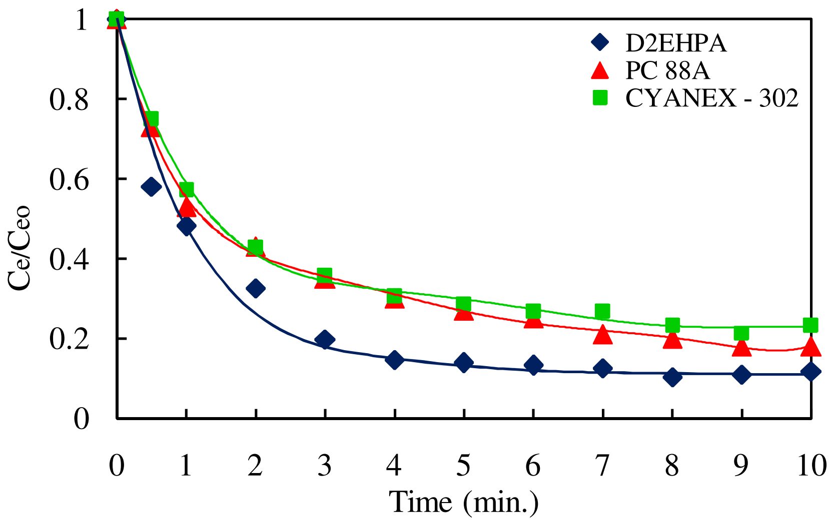


Fig. 5.34: Extraction of zinc using organophosphorous extractants at Cc=10% (v/v) (pH=4.5, ϕ=0.5, Cio=1.5 M, Ceo=1000 mg/L, TR=1:6).

5.7 Zinc extraction using mixture of organophosphorous extractants into ELMs

The transfer of metal cations from aqueous phase into an organic phase most often requires the use of an extractant capable of satisfying the salvation and coordination preferences of the cationic solute. In some cases single extractant molecule can accomplish this task while in others several extractant molecules must cooperate to affect this phase transfer of the cation. This aspect is quite often encountered in the extraction of cations by chelating and / or acidic extractants and may involve formation of complexes in which the primary coordination sphere of the cation includes sufficient deprotonated extractant molecules to maintain electroneutrality and one or more neutral extractant molecules to saturate the coordination environment of the cation.

$$M^{m+} + pHA_{org} \leftrightarrow M\,(A)_m \,.\, (p-m)\,HA_{org} + mH^+$$

Such self adduct formation makes the complex more organophilic but is often highly sensitive to steric repulsions due to the bulky organic frame work of the extractant that imparts organophilicity to the extractant (Bond et al. 2000).

As an alternative two extractant that fulfill different objectives in the extraction process may be used, one extractant complexes the metal cation and neutralizes charge while another, perhaps less sterically demanding, extractant may serve to replace water or to occupy open coordination sites. In this way, two extractants cooperate to increase the extraction, which is greater than the sum of each extractant operating independently. Usually combinations of acidic and neutral extractants have been widely tried out for their synergistic effects whereas the combination of two acidic extractants is less common (Andrade and Elizalde 2005).

In the current investigation combinations of the three organophosphorous extractants, which were earlier individually used as carrier in ELM systems was investigated for zinc recovery from aqueous streams into ELMs. The emulsions were formulated with internal phase volume fraction of 0.5, strip acid concentration of 1.5 M, surfactant concentration 3 wt% of oil phase. The pH of operation was 4.5 and emulsion was dispersed at agitation speed of 150 rpm, treat ratio was 1:6 and the feed concentration was 1000 mg/L of zinc.

Extraction of zinc was explored with six different combinations of organophosphorous extractants used as carriers namely (a) 5% (v/v) D2EHPA + 2% (v/v) PC 88A, (b) 5% (v/v) D2EHPA + 2% (v/v) CYANEX 302, (c) 5% (v/v) PC 88A + 2% (v/v) D2EHPA, (d) 5% (v/v) PC 88A + 2% (v/v) CYANEX 302, (e) 5% (v/v) CYANEX 302 + 2% (v/v) D2EHPA, (f) 5% (v/v) CYANEX 302 + 2% (v/v) PC 88A, these combinations were denoted as SE1, SE2, SE3, SE4, SE5 and SE6 respectively. Except for the carrier type and concentration all other emulsion parameters and process parameters remained invariant.

The results of the extraction runs with the extractant SE1 (5% (v/v) D2EHPA + 2% (v/v) PC 88A) and SE2 (5% (v/v) D2EHPA + 2% (v/v) CYANEX 302) are shown in Fig 5.35. It is observed that with both these extractants quantitative extraction of solute takes place but the rate of zinc extraction with SE1 was considerably faster than with SE2. Using SE1 as carrier quantitative extraction took place in only five minutes while with SE2 extraction was achieved in 8 minutes. In the same figure the extraction plots with 5% (v/v) and 10% (v/v) D2EHPA under identical conditions are shown, it is observed that in the time frame that SE1 achieves quantitative removal of zinc, 5% (v/v) D2EHPA achieves only ~ 55% removal and 10% (v/v) D2EHPA achieves 85% removal. In the same time frame 5% (v/v) PC 88A achieves about 38% zinc removal under identical conditions as seen from Fig. 5.36. Hence,

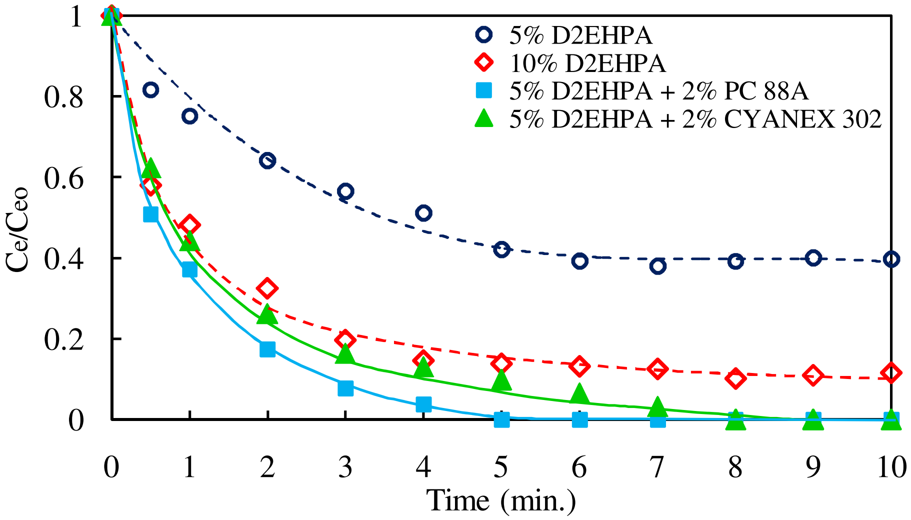


Fig. 5.35: Kinetics of zinc extraction into ELMs using synergistic extractants SE1 and SE2

it can be expected that the combination of 5% (v/v) D2EHPA and 5% (v/v) PC 88A could give a maximum of ~ 93% removal (neglecting the decline in concentration gradients and other physicochemical factors that are intrinsic to such extractions) which appears to be better than that obtained with D2EHPA having 10% (v/v) concentration. The performance of SE1 supersedes all these anticipations, with just 7% (v/v) total extractant content it gives far better results. Therefore, it is clear that this combination is a synergistic mixture although total characterization of the extractant mixture such as the pH_{50} shift and the synergistic coefficients were not evaluated but these results itself gives a qualitative judgment regarding the synergistic nature based on actual performance data.

Same is the case with the SE2 combination which supersedes the performance of 10% (v/v) D2EHPA and also gives a better performance than the plausible combination of 5% (v/v) D2EHPA and 5% (v/v) CYANEX 302 with only a net 7% (v/v) extractant. It is interesting to observe that 50% removal time of SE1 and SE2 are nearly identical therefore it is unlikely that the difference in the performance of these extractants stem from differences in loading, it appears that the difference then results from the stripping behavior that is in consonance with the slow rates of stripping of CYANEX 302.

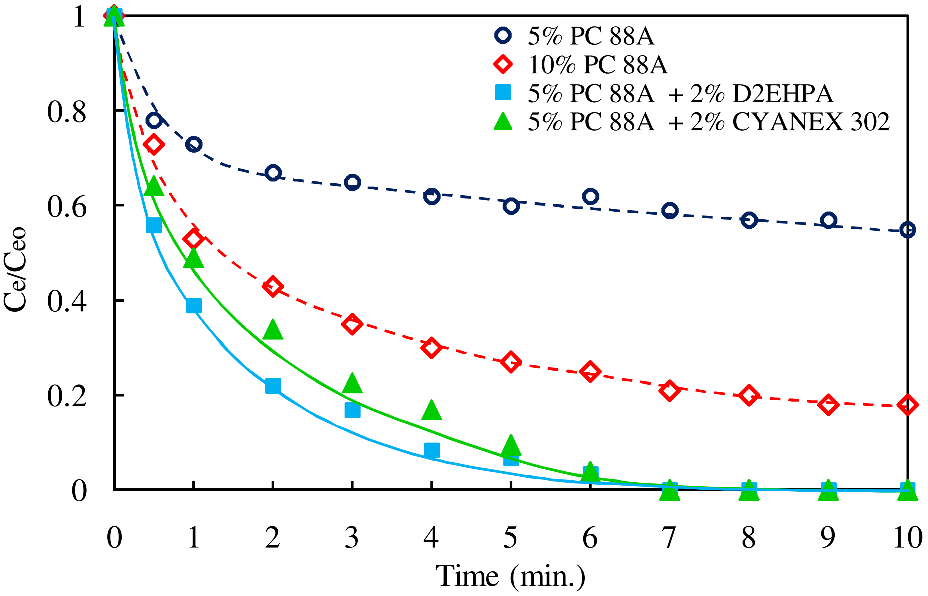


Fig. 5.36: Kinetics of zinc extraction into ELMs using synergistic extractants SE3 and SE4

The extractant combination of 5% (v/v) PC 88A with 2% (v/v) D2EHPA denoted as SE3 and 5% (v/v) PC 88A and 2% (v/v) CYANEX 302 denoted as SE4 also showed synergy for zinc extraction as seen in Fig. 5.37 Both SE3 and SE4 gave nearly same results and achieved quantitative extraction in seven minutes time. In the same time interval 10% (v/v) PC 88A account for only 80% zinc extraction and is unable to extract zinc any further. Independently 5% (v/v) PC 88A and 5% (v/v) CYANEX 302 in 7 minutes recover 38% and 58% zinc respectively as seen in Fig. 5.36 and Fig. 5.37. Hence, the performance of both SE3 and SE4 exceeds the performance of 10% (v/v) PC 88A as well as a plausible combination of PC 88A with either D2EHPA or CYANEX 302 in proportion of 5% (v/v) of each using only 7% net (v/v) concentration of the extractant mixture as carrier thereby justifying the extractant mixtures as synergistic mixture.

As discussed earlier to achieve synergy two extractants perform two different tasks one neutralizes the charge while the other solvates and aids the transfer process. Earlier investigators studying the synergy between chelating and acidic extractants have shown that PC 88A has strong tendency to function as a phase transfer agent. In the current context where both extractants are acidic extractants it is likely that mixed complexes tend to form.

The mixed extractant system involving CYANEX 302 as the major component with D2EHPA and PC 88A as the other component also showed synergy for the extraction of zinc ions from feed solution into ELMs as seen in Fig. 5.36 . The performance of SE5 and SE6 mixtures exceeded the performance of 10% (v/v) CYANEX 302 that recorded only 78% extraction of zinc in 10 min.

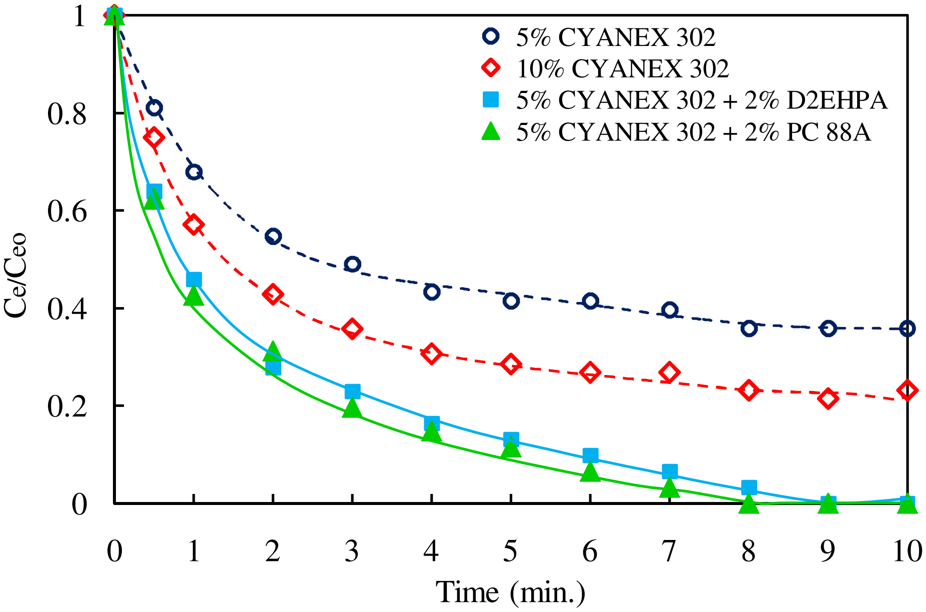


Fig. 5.37: Kinetics of zinc extraction into ELMs using synergistic extractants SE5 and SE6

In contrast SE5 recorded quantitative extraction in nine minutes and SE6 the extractant mixture of 5% CYANEX 302 with 2% PC 88A attained quantitative extraction in just eight minutes. SE5 performed superior to the cumulative amount of zinc extracted independently by 5% CYANEX 302 and 5% D2EHPA in nine minutes time similarly SE6 performed better than the cumulative amount of zinc extracted independently by 5% CYANEX 302 and 5% PC88A as can be figured out from Table 5.4.

These results indicate that mixing the two organophosphorous extractants in small proportion, where the main extractant has 5% (v/v) concentration and the second extractant has 2% (v/v) concentration i.e. together only 7% net concentration (v/v) in the extractant mixture results in a synergistic mixture that facilitates the extraction – stripping process in the ELMs. It can be observed from Table 5.4 that PC 88A as the second extractant induces greater synergy which could be due to the role of PC 88A as a phase transfer agent as well as its facilitating the stripping process because of its weak complex formation with the metal ion. However, this aspect needs to be thoroughly investigated.

Table 5. 4: Fractional extraction of zinc into ELMs using synergistic extractant mixtures as carriers

Time (min.)	5% D2EHPA	10% D2EHPA	SE1	SE2	5% PC 88A	10% PC 88A	SE3	SE4	5% CYANEX 302	10% CYANEX 302	SE5	SE6
0	0	0	0	0	0	0	0	0	0	0	0	0
0.5	0.18	0.42	0.49	0.38	0.22	0.27	0.44	0.36	0.19	0.25	0.36	0.38
1	0.25	0.52	0.63	0.56	0.27	0.47	0.61	0.51	0.32	0.43	0.54	0.57
2	0.36	0.67	0.83	0.74	0.33	0.57	0.78	0.66	0.45	0.57	0.72	0.69
3	0.43	0.80	0.92	0.84	0.35	0.65	0.83	0.77	0.51	0.64	0.77	0.80
4	0.49	0.85	0.96	0.87	0.38	0.70	0.92	0.83	0.57	0.69	0.84	0.85
5	0.58	0.86	1	0.90	0.40	0.73	0.93	0.91	0.59	0.71	0.87	0.89
6	0.61	0.87	1	0.93	0.38	0.75	0.97	0.96	0.59	0.73	0.90	0.93
7	0.62	0.87	1	0.97	0.41	0.79	1	1	0.6	0.73	0.93	0.97
8	0.61	0.90	1	1	0.43	0.80	1	1	0.64	0.77	0.97	1
9	0.60	0.89	1	1	0.43	0.82	1	1	0.64	0.79	1	1
10	0.60	0.88	1	1	0.45	0.82	1	1	0.64	0.77	1	1

SE1 (5% D2EHPA + 2% PC 88A), SE2 (5% D2EHPA + 2% CYANEX 302), SE3 (5% PC 88A + 2% D2EHPA)
SE4 (5% PC 88A + 2% CYANEX 302), SE5 (5% CYANEX 302 + 2% D2EHPA), SE6 (5% CYANEX 302 + 2% PC 88A)

On the whole the use of organophosphorous acid mixtures as carrier helped us achieve quantitative removal of zinc from the feed solutions at reasonable rates one of the objectives with which we initiated this study. Further the results establish the efficacy of ELMs as a vehicle for intensification of the extraction of zinc using commercially available extractants as carriers.

5.8 IR spectroscopy of zinc – extractant complexes

The bonding of Zn with the organophosphorous extractants in the organic phase was revealed by comparing the FTIR spectra of the native extractant in kerosene with the spectra obtained for zinc loaded extractant in kerosene. The concentration of extractant was maintained constant 10% (v/v) for obtaining the spectra for unloaded as well as Zn loaded samples.

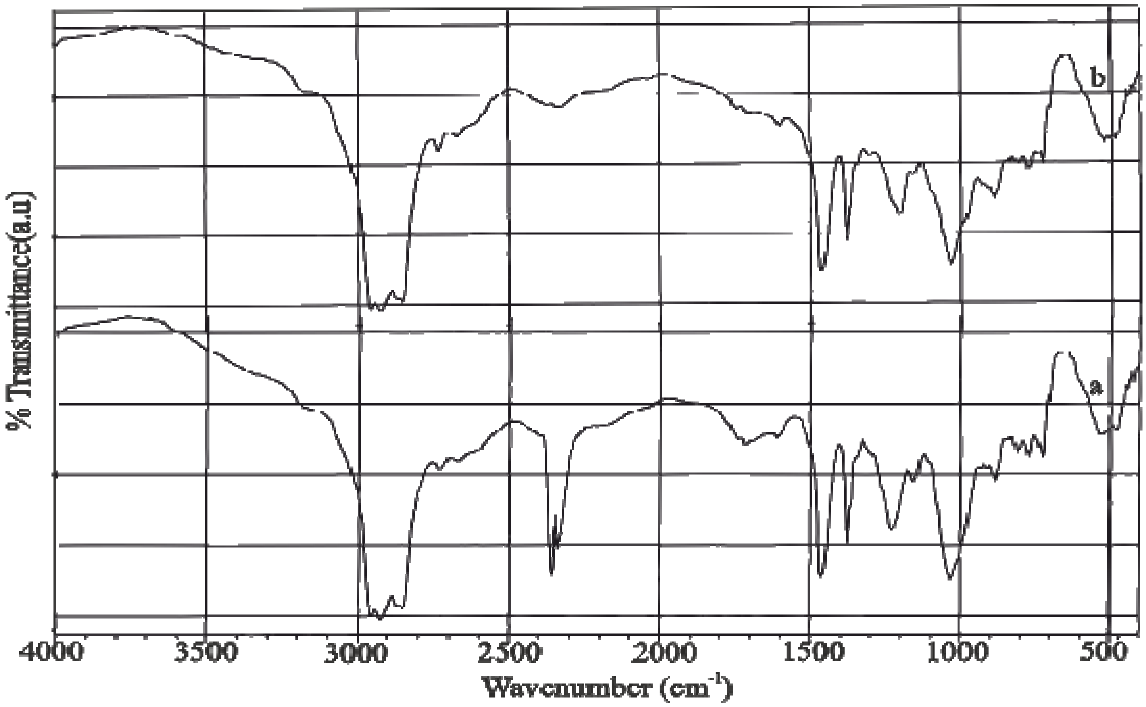


Fig. 5.38: FTIR spectra of (a) 10% (v/v) D2EHPA in kerosene, (b) 10% (v/v) D2EHPA loaded with zinc in kerosene

The IR spectra of D2EHPA in kerosene is shown in Fig 5.38(a) highlights the presence of the main groups such as P=O, P – O – C, P – O – H and OH (Silverstien *et al.* 1991) P – O – H showed an intense band at 1033.8 cm^{-1}, P=O stretching frequency was observed at 1230.63 cm^{-1}. The OH^{-} bending vibration is observed at ~1690 cm^{-1}. In addition intense bands of asymmetric carbon (γ_{as}) and symmetric carbon (γ_{sy}) associated with the stretching vibrations of CH bands in CH_2 and CH_3 are observed at 2926 cm^{-1} and 2850 cm^{-1}.The bands at 1464.7 cm^{-1}and 1377 cm^{-1} are associated with bending vibrations of these groups similar spectral patterns were observed by Sainz-Diaz *et al.* (1996).

After metal binding the strong band at 2343 cm^{-1} assigned to the OH (included in P-O-H) is not found indicating coordination with metal via deprotonation as seen in Fig. 5.38(b). Further there is a shift of the P=O from 1230.6 to 1203.6 cm^{-1}, such shift of band to lower wave numbers indicates coordination with the metal.

The characteristic bands of PC 88A (Huang *et al.* 1992, Ma *et al.* 1981) are the P – C band at 869.9cm^{-1}, P – O – C band at 983.7 cm^{-1}, P – OH band at 1033.8 cm^{-1} and P=O band at 1195.9 cm^{-1} all these bands are seen in Fig. 5.39(a). In addition there is abroad OH band at ~1680 cm^{-1}, the bands of asymmetric carbon (γ_{as}) and symmetric carbon (γ_{sy}) associated with the stretching vibrations of CH bands in CH_2 and CH_3 are observed at 2956 cm^{-1} and 2856 cm^{-1}.The bands at 1460 $cm^{-1}$and 1377 cm^{-1} are associated with bending vibrations of these groups.

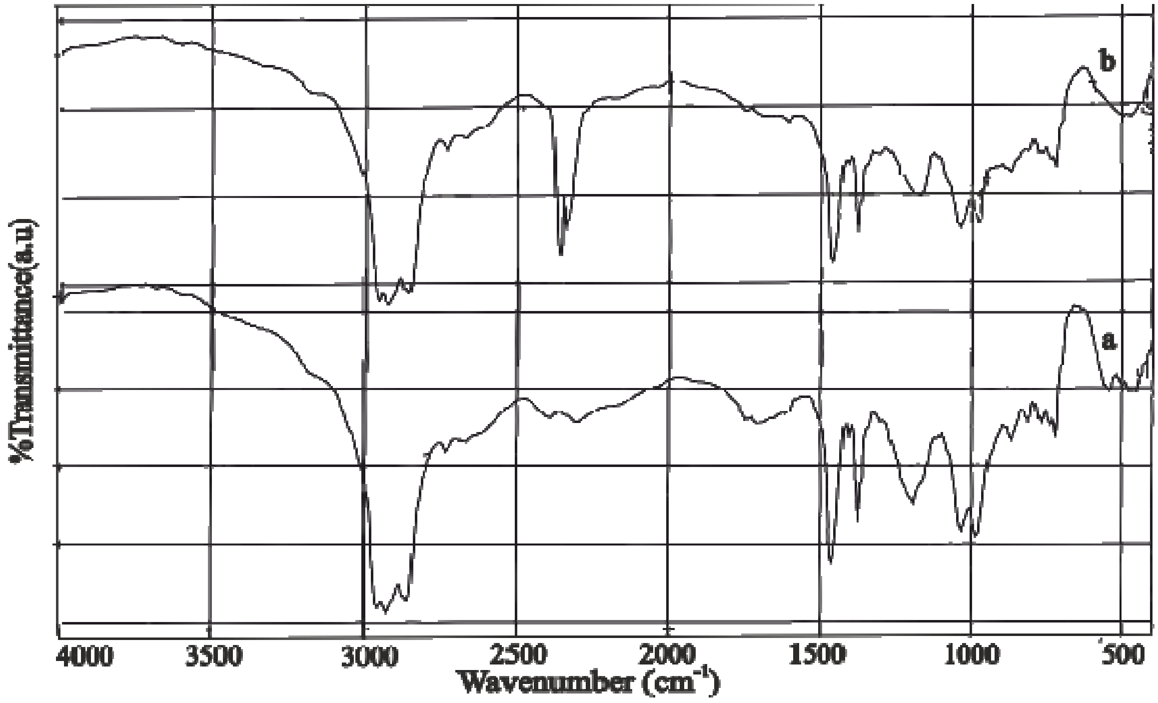


Fig. 5.39: FTIR spectra of (a) 10% (v/v) PC 88A in kerosene, (b) 10% (v/v) PC 88A loaded with zinc in kerosene

The phosphoryl bond gets highly affected when extractant binds with zinc, the IR spectra of Zn loaded PC 88A shows two P=O bands at 1188 and 1170.8 cm^{-1} corresponding to free and metal bound P=O as seen in Fig. 5.39(b).

It is reported that CYANEX 302 available commercially contains approximately 85% active reagent i.e.$R_2P(S)OH$ [bis (2,4,4-trimethyl pentyl) monothiophosphinic acid] it also contains about 12% R_3PO [tris (2,4,4-trimethyl pentyl)phosphine oxide] and small quantities of $R_2P(O)OH$, $R_3P(S)SH$ etc. The presence of impurities complicates the spectra although their presence does not affect any of the conclusions. CYANEX 302 exists as two structural tautomers, in solvents the thino form is predominant existing in ~ 90% times while the thiol form is scarce (Menoyo *et al.* 2002, Silverstein *et al.* 1991). Therefore the characteristic bands of CYANEX 302 are P=S, P – OH and P– C which are seen in Fig. 5.40(a) and Fig. 5.40(b). The band at 597.95 $cm^{-1}$is due to the P=S moiety and this undergoes a shift due to coordination with zinc from 597.95 to 582.52 cm^{-1}. The spectrum also shows the absorption characteristics of the P=S group, the doublet at 738.7 and723.3 cm^{-1} and the doublet at 607 and 597.9 cm^{-1}. Nyquist (1969) suggested that these bands occur as doublet due to the existence of rotational isomers.

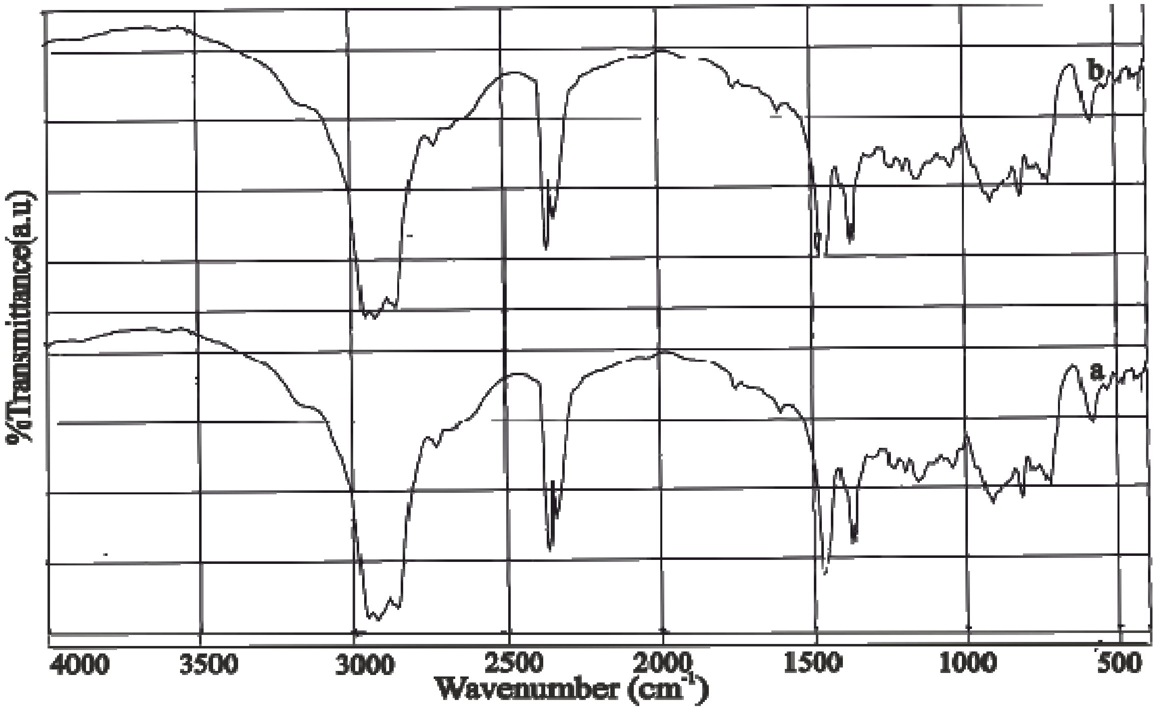


Fig. 5.40: FTIR spectra of (a) 10% (v/v) CYANEX 302 in kerosene, (b) 10% (v/v) CYANEX 302 loaded with zinc in kerosene

Absence of a band in 2600 – 2500 cm^{-1} region indicates absence of S – H stretch hence rules out a thiol structure. The strong absorption band at 918 cm^{-1} corresponds to P – O stretching vibration in P – OH band. The band at 820 cm^{-1} corresponds to P – C stretch vibration. The bands at 2950 to 2800 cm^{-1} are the CH stretching frequencies and they remain unperturbed because they do not participate in the coordination.

IR of extractant mixtures that led to quantitative extraction of zinc from sulfate solutions was also performed to get a clue on the bonding patterns that give rise to the synergy observed in these cases. The mixed extractants involved were 5% D2EHPA + 2% PC 88A, 5% D2EHPA + 2% CYANEX 302, 5% PC 88A + 2% D2EHPA, 5% PC 88A + 2% CYANEX 302, 5% CYANEX 302 + 2% D2EHPA, 5% CYANEX 302 + 2% PC 88A (all expressed in volume percent in kerosene). The IR spectra of these six combinations loaded with zinc are shown in Fig. 5. 41.

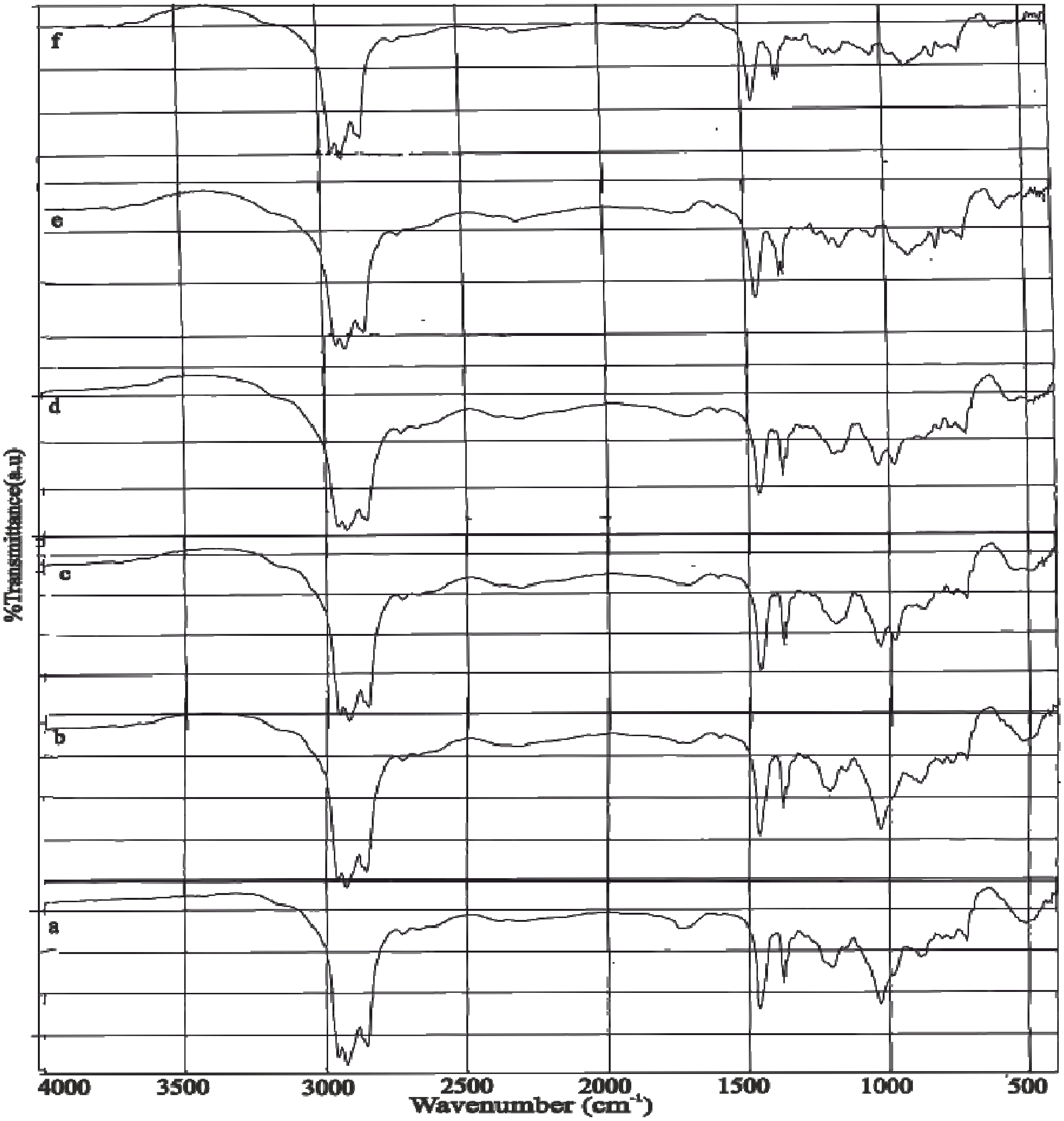


Fig. 5.41: IR spectra of combinations of organophosphorous extractants loaded with zinc

(a) 5% D2EHPA + 2% PC 88A, (b) 5% D2EHPA + 2% CYANEX 302, (c) 5% PC 88A + 2% D2EHPA, (d) 5% PC 88A + 2% CYANEX 302, (e) 5% CYANEX 302 + 2% D2EHPA, (f) 5% CYANEX 302 + 2% PC 88A

The IR of mixed extractants loaded with zinc shown in Fig. 5.41 reveals that the P=O bond is mostly affected in all the cases. In mixtures of 5% D2EHPA and 2% PC 88A it is seen that the P=O bond appears at 1203.6 cm^{-1}, as was observed earlier in Fig. 5.41(b) the IR spectra of Zn bonding with 10% (v/v) D2EHPA. However the P=O band of PC 88A that appeared at 1170 cm^{-1} for zinc bound complex is not seen. It is likely that this band could have been masked by the P=O band of D2EHPA since the low concentration of PC 88A would have reduced the intensity of this band considerably.

The IR spectra of 5% (v/v) PC 88A and 2% (v/v) D2EHPA shows the characteristic PC 88A P=O bands at 1192 and 1170.8 cm^{-1} for free extractant and the bound extractant but the bound P=O band of D2EHPA at 1203.6 cm^{-1} is not seen. The IR spectra of zinc loaded in a mixture of 5% (v/v) D2EHPA and 2% (v/v) CYANEX 302 shows a shift in the P=O band from its unbound value of 1230 to 1211.3 cm^{-1}, a weak P=S band is seen at ~ 600 cm^{-1}. The spectra of 5% (v/v) CYANEX 302 and 2% (v/v) D2EHPA loaded with zinc shows the P=S bands at 580.6 cm^{-1} but with low stretching.

The IR spectra of Zn loaded in 5% CYANEX 302 and 2% PC 88A shows the characteristic P=O bands at 1197.8 cm^{-1} for free extractant that shifts to 1159 cm^{-1} on bonding with zinc. The P=S band of CYANEX appears at 580.6 cm^{-1}. The spectra of zinc loaded in 5% PC 88A and 2% CYANEX 302 shows the P=O band at 1166.9 cm^{-1}, while the P=S band is a broad one at 549.7 cm^{-1}.

It is interesting to note that the characteristic bands of the three extractants appear even when they are in binary pairs indicating there is no interaction between the extractants. In view of this it is likely that the synergy observed in the ELM extractions stems from the stripping behavior rather than the loading patterns. This area needs to be explored further for quantitative assessment.

5.9 Conclusions

Work on zinc extraction using organophosphorous extractants as carriers in ELMs was initiated with the objective of achieving quantitative extraction of the zinc and defining the parametric space required for fulfilling this objective. Quantitative extraction could be achieved using mixed extractants exploiting the synergy between the extractants for removal of metal species. The significant findings of this investigation are summarized below:-

pH isotherms of the three extractants used as carrier in this investigation showed that the acidity of the extractants were in the order D2EHPA > PC 88A > CYANEX 302. Therefore D2EHPA had the advantage of operating in a wider and more acidic environment in comparison with the other two extractants.

The effect of various parameters on zinc extraction using each of these extractant as carrier in ELMs was explored independently. In general the results indicated that loading of zinc is the dominant process governing extraction therefore the conditions that favor loading viz. increase in carrier concentration, increase in treat ratio, and appropriate pH value lead to a greater solute removal. Increase in the internal phase volume fraction that increases storage capacity in the emulsion but reduces carrier content in the system was found to be deleterious to extraction of zinc, sometimes this effect was drastic.

Comparing the three extractants revealed unique behavioral features which were not recognized within the parameter space of any single extractant, for example the similarities of extraction patterns of PC 88A and CYANEX 302 are widely observed, only in the case of extraction at pH 2.5 they show distinctly separate extraction profiles. Such distinctly different extraction profiles were also observed for zinc extraction at pH 4.5 with feed concentration of 3000 mg/L and also during the investigation on the effect of treat ratios. Such insights on the behavior of extractants provide valuable information useful in selection of extractants.

None of the extractants when used alone achieved quantitative removal of zinc while the combination of organophosphorous extractants D2EHPA + PC88A, D2EHPA + CYANEX 302 and PC 88A + CYANEX 302 displayed synergy and achieved quantitative removal of zinc in all six cases investigated in this study, the combination of D2EHPA + PC 88A displayed the most intense synergy and achieved quantitative removal in just 5 minutes. The objective with which the investigation was initiated was fulfilled due to the synergy of the extractants.

The nature of bonding of metal with the extractants was explored using IR spectroscopy. IR spectra revealed that in D2EHPA and PC 88A the P=O bonds while in CYANEX 302 the P=S bonds get most affected when extractants bond with zinc independently. The same was true also for extractant mixtures. It appears from this investigation that the extractants do not interact with each other but only facilitate each other for enhanced metal loading into ELMs.

CHAPTER 6
SUMMARY AND CONCLUSIONS

6.1 Introduction

Heavy metals pose a potential environmental hazard to living organisms due to the inherent toxicity, their tendency of bioaccumulation, coupled with associated carcinogenicity and mutagenicity. Mining, industrial activity, other anthropogenic activity as well as natural causes release heavy metals into the ecosphere. It is imperative on the part of civil society to take necessary steps to eliminate heavy metals from wastewater streams prior to their disposal so that water bodies do not get contaminated with such heavy metals.

There are numerous techniques available to treat heavy metal containing wastes but most of them are non selective and become uneconomical at low concentration levels at which the toxicity of heavy metal is retained. Emulsion liquid membrane technology is a novel technique that has considerable potential to treat targeted heavy metals with high selectivity and recover them even at very low concentration levels at a moderate cost.

This study investigates the extraction and removal of metals such as copper, zinc and nickel from aqueous streams individually as well as in binary combinations from ammoniacal media and zinc from acidic media as well using emulsion liquid membranes that are benchmarked to remain stable at the given operating conditions. The significant findings are reported and conclusions are listed below.

6.2 Emulsion formulation and characterization

Stability is the hallmark of sustained industrial activity and heavy metal recovery using ELMs need to be incorporated in its perimeter. Since emulsions are inherently unstable systems therefore, particular care needs to be taken in their formulation and use during process operation so that they retain their stability. The *Achilles Heel* of ELM technology has been instability and many industrial processes avoided this technology on account of this weakness.

In this study W/O emulsions were formulated by using kerosene as the oil membrane phase, sulfuric acid in the internal stripping phase with Span 80 as the emulsifier. The art of mixing was perfected that gave stable emulsions for the operations. The emulsions were characterized by their viscosity, internal drop sizes and interfacial tension. Emulsion globule sizes obtained after dispersion of the emulsion at 150 rpm were also measured in some cases.

6.3 Extraction of heavy metals from ammoniacal solutions

Ammoniacal leaching of ores is an age old technique for recovery of metal values; this technique has again come in focus with the idea to process deep sea nodules for recovery of metals such as nickel, manganese, zinc etc. Ammoniacal leaching is also practiced in metal recovery from electronic printed circuit wastes. Recovery of metal values from ammoniacal media using ELMs is largely unexplored territory. In this study for the first time commercial chelating extractants were used as carriers to recover metals such as copper, zinc and nickel from ammoniacal solutions. Co-extraction of copper - zinc and copper – nickel were also investigated and the possibility of selective separation was explored.

It was found that for all the systems studied the feed phase pH=8.1 were appropriate for extraction moreover, ammonia transport in the ELMs was not encountered in any run. Copper extraction was very fast and quantitative extraction was observed in many cases, loading of solute in the membrane phase governed the extraction rates. Solvent extraction studies indicated that with zinc the stripping of the LIX 84I complex with acid was slower in comparison to loading. Experiments on the co-extraction of copper and zinc and their stripping indicate that zinc loads in the oil phase to a greater extent in the presence of copper. Zinc strips faster than copper from the oil phase when the zinc concentration is comparable or more than copper.

Effect of emulsion parameters in general showed similar trends, increase of internal phase acid concentration in general was deleterious to extraction due to problems of dispersion associated with very viscous emulsions and also due to decline of surface areas for mass transfer because of increase in the internal droplet sizes of the emulsion. Increase in internal phase acid concentration had solute specific effects for nickel extraction 1.0 M concentration was optimal and there was serious decline on increase of concentration but for copper extraction 1.5 M was appropriate in view of the strongly bonded complex of copper with the extractant. Increase in carrier concentration was always favorable to the extraction.

Process parameters such as treat ratio of emulsion to feed was in general advantageous to extraction for treat ratio of 1:5 in comparison to 1:10 due to increase in carrier concentration and the surface areas for mass transfer. Increase in feed concentration always resulted in greater amount of solute being loaded by the emulsion although fraction loaded declined.

During co- extraction of copper and zinc using ELMs it was observed that the overall copper extraction rates were much larger than zinc. Loading of copper dictates the separation. ELMs with LIX 84I show preference for selective removal of copper from zinc with separation factor β (Cu/Zn) = 3.5.

A new dimension was opened in ELM studies starting with nickel extraction and extended to co-extraction of copper and nickel from ammoniacal media when the W/O emulsions were disintegrated after the extraction and the inner acid phase was analyzed to measure the amount of metal stripped. It was interesting to find that in most cases for Ni extraction from ammoniacal media the extent of stripping in 10 minutes duration was 55% of the solute extracted. The rate of copper extraction was much greater than the rate of nickel extraction. In the experimental range of concentrations investigated copper could be quantitatively loaded in the emulsion even when its concentration was very large. Nickel loading declined in the presence of copper, further copper stripped to a far greater extent in the internal phase of the emulsion in comparison to nickel. It was interesting to find that the amount of copper stripped in the internal phase was equivalent to the amount of nickel uptake by the ELMs.

The separation factors for Cu – Ni separation increases with increasing initial copper concentration in the feed and had a maximum value of 2.91 in the concentration range studied. It is concluded that ELM technology could be used for selective removal of copper from copper–nickel mixtures as well as from copper-zinc mixtures in ammoniacal media.

6.4 Extraction of zinc from sulphate solutions

The first commercial plant using ELM technology for metal recovery was commissioned in Austria for zinc removal from rayon wastes. Although industrialized in 1980’s this technology did not proliferate at other sites for Zn removal because of numerous problems that needed to be addressed, one requirement was to ensure almost quantitative extraction using extractants commercially available. This problem is addressed Chapter 5 using commercially available organophosphorous extractants.

Three organophosphorous acids commercially named D2EHPA, PC 88A and CYANEX 302 were investigated for zinc removal from sulphate media. The parameter spaces for each of these extractants were explored and their interaction for zinc removal was also investigated. Initially pH isotherms for each of these extractants was generated and it was found that the acidity of the extractants were in the order D2EHPA > PC 88A > CYANEX 302. Therefore D2EHPA had the advantage of operating in a wider and acidic environment in comparison with the other two extractants.

In general the results indicated that loading of zinc is the dominant process governing extraction therefore all conditions that favour loading viz. increase in carrier concentration, increase in treat ratio, and appropriate pH value lead to a greater extent of solute removal. Increase in the internal phase volume fraction that increases storage capacity of the emulsion but reduces carrier content in the system was found to be deleterious to extraction of zinc sometimes the effect was rather drastic.

Comparing the three extractants revealed unique aspects of behavior that were not cognizable when dealing with the parameter space of any single extractant, for example the similarities of extraction patterns of PC 88A and CYANEX 302 are widely observed, only in the case of extraction at pH 2.5 they show distinctly separate extraction profiles. Similarly such distinctly different extraction profiles was observed for zinc extraction at pH 4.5 and Cio of 3000 mg/L and also during the investigation on the effect of treat ratios. Such insights on the behavior of extractants provide valuable information that is useful in selection of extractants.

None of the extractants when used alone could achieve quantitative removal of zinc, since this was one of the goal of this study, attempts were made to achieve quantitative extraction by using mixture of extractants as carrier in ELMs. It is known that often two extractants cooperate to increase the extraction which is greater than the sum total of each extractant operating independently, such mixture of extractants are called synergistic mixtures. The combination of organophosphorous extractants D2EHPA + PC88A, D2EHPA + CYANEX 302 and PC 88A + CYANEX 302 displayed synergy and achieved quantitative removal of zinc in all cases, the combination of D2EHPA + PC 88A displayed the most intense synergy and achieved quantitative removal in just 5 minutes. The objective with which the investigation was initiated was fulfilled due to the synergy of the extractants.

The nature of bonding of metal with the extractants was explored using IR spectroscopy. IR spectra revealed that in D2EHPA and PC 88A the P=O bonds while in CYANEX 302 the P=S bonds get most affected when extractants bond with zinc independently. The same was true also for extractant mixtures. It appears from this investigation that the extractants do not interact with each other but only facilitate each other for enhanced metal loading into ELMs.

6.5 Scope for future work

Scientific investigations are undertaken to provide answers but they also raise many new questions that enlarges the work. Emulsion liquid membrane separation is still a nascent area and there is ample scope for work in future. We envisage that extraction using synergistic extractants need to be put in greater focus, some areas related the current investigation that needs to be addressed in future are the following:

A more detailed study on the synergistic systems involving D2EHPA, PC 88A and CYANEX 302 need to be undertaken and the aspects of loading and stripping need to be investigated separately to understand the reason of such synergy. Synergistic coefficients and ΔpH_{50} should be evaluated to quantify the synergy.

The effect of internal phase volume fraction of the emulsion on the rates of extraction should be investigated more intensively to identify the factor causing such deleterious effect as that observed with PC 88A and CYANEX 302.

A method needs to be developed to split the emulsion without altering the distribution of the solute existing in the membrane phase and the internal phase. If this can be done much deeper insight on the ELM behavior can be attained.

Extraction from ammoniacal media needs to be expanded to other metal species as well. Copper and zinc co-extraction exhibited a pattern of synergy, this aspect needs to be explored further and its implications on removal of metals from actual waste streams or run of mine waters that contain salts of different metals.

Mathematical modeling of the entire extraction process including process chemistry, speciation dynamics, metal recovery, uptake by emulsions etc. need to be quantified and predicted.

This study in a way is a humble beginning in the area of extraction of metals from ammoniacal media and the synergistic extraction of metals using ELMs. It is hoped that these investigation will be stepping stone for not only more profound investigations in future but also pave way for greater commercialization of the ELM technologies.

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