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SELECTIVE EMULSION LIQUID MEMBRANE EXTRACTION OF SILVER FROM LIQUID PHOTOGRAPHIC WASTE INDUSTRIES

(PENGEKSTRAKAN EMULSI SELAPUT CECAIR TERPILIH LOGAM PERAK DARI SISA INDUSTRI FOROGRAFI)

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ABSTRACT

SELECTIVE EMULSION LIQUID MEMBRANE EXTRACTION OF SILVER FROM PHOTOGRAPHIC WASTE INDUSTRIES

(Keywords: Emulsion liquid membrane, extraction, photographic waste, silver)

The field of liquid membrane technology is currently undergoing a rapid expansion in research as well as its application as an industrial separation process. Liquid membrane can be manipulated to selectively separate a specific solute from a mixture and even to extract a solute against its concentration gradient. A liquid membrane system comprises of three liquid phases; feed phase, liquid membrane organic phase and receiving phase. Liquid membrane can be prepared using support or as emulsion (unsupported) liquid membrane. Emulsion liquid membrane is a liquid membrane in which the membrane phase of an emulsion is dispersed into the feed phase to be treated. This method was investigated as an alternative process for the recovery of silver from photographic waste, which contains various metals ions such as silver, iron, sodium and potassium. The important parameters governing the extraction process of silver such as agitation speed, homogenizer speed, surfactant and carrier concentrations, type of diluents, treat ratio and types of stripping solution were investigated. This process has been conducted in a batch system using a mixer-settler. The results show that the mobile carrier Cyanex 302 is selective towards silver and almost completely extract silver over the other metals that existed in the photographic waste. The optimum silver extraction was obtained by using 0.03 M Cyanex 302, 3 % (w/v) Span 80, 250 rpm stirring speed, 1.0 M thiourea in 1.0 M H_2SO_4 stripping agent, 1:5 of treat ratio, and kerosene as a diluent. The experimental result also shows that the emulsion liquid membrane system could be recycled twice having 80% of silver was extracted. In addition, theoretical studies show that the developed model could predict the extraction performance of the system understudied as obtained from experimental data.

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ABSTRAK

PENGEKSTRAKAN EMULSI SELAPUT CECAIR TERPILIH LOGAM PERAK DARI SISA INDUSTRI PHOTOGRAFI

(Kata kunci: Emulsi selaput cecair, pengekstrakan, sisa fotografi, logam perak)

Pada masa kini, bidang teknologi membran cecair telah berkembang dengan pesat di bidang penyelidikan dan juga penggunaannya sebagai proses pemisahan di industri. Membran cecair boleh bertindak memisahkan bahan larut secara terpilih daripada campuran di samping boleh mengekstrak bahan larut melalui kecerunan kepekatan bahan larut tersebut. Sistem membran cecair terdiri daripada tiga fasa cecair; fasa suapan, fasa organik membran cecair dan fasa penerima. Membran cecair boleh disediakan dalam dua bentuk iaitu membran cecair bersokong atau berbentuk emulsi (tanpa sokongan). Sistem emulsi membran cecair adalah merupakan membran cecair dalam mana diserakkan ke dalam fasa suapan yang akan dirawat. Kaedah ini telah dikaji sebagai kaedah alternatif bagi perolehan semula logam perak daripada sisa fotografik yang mengandungi berbagai jenis ion logam seperti perak, besi, natrium dan kalium. Parameter penting yang menentukan kemampuan pengekstrakan logam perak seperti kelajuan penggodakan, kelajuan homogenasi, kepekatan pengemulsi dan pembawa, jenis pelarut organik, nisbah rawatan bagi emulsi kepada fasa suapan dan jenis larutan pelucut dikaji. Proses ini telah dijalankan dengan menggunakan sistem pengaduk-pemisah berkelompok. Keputusan menunjukkan pembawa Cyanex 302 adalah terpilih terhadap logam perak dan hampir mengekstrak sempurna logam perak berbanding logam lain yang terdapat di dalam sisa fotografik. Pengekstrakan optima logam perak diperolehi dengan menggunakan 0.03 M Cyanex 302, 3% (w/v) Span 80, kelajuan pengadukan 250 rpm, agen pelucut 1.0 M thiourea dalam 1.0 M H_2SO_4, 1:5 nisbah rawatan, dan kerosen sebagai pelarut organik. Keputusan ujikaji juga menunjukkan bahawa membran cecair juga berkebolehan dikitar semula sebanyak dua kali dengan 80% pengekstrakan logam perak. Tambahan lagi, pengkajian secara teori menunjukkan model yang dibangunkan boleh meramalkan prestasi pengekstrakan bagi sistem yang dikaji berasaskan data yang diperolehi dari ujikaji.

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Ag	- Silver
$[Ag_{ext}]$	- Silver concentration in external phase
$[Ag_{int}]$	- Silver concentration in internal phase
$[Ag_{mem}]$	- Silver concentration in membrane phase
$C_e(t)$	- Concentration of solute in external phase
C_{eo}	- Initial concentration of solute in external phase
$C_{ex,o}$	- Initial concentration of solute in external phase
$C_{ex,f}$	- Final concentration of solute in external phase
C_e/C_{eo}	- Ratio of concentration of silver to initial concentration in external phase
$C_{A,III}$	- Concentration of solute in the external phase (mol/l).
$C_{H,III}$	- Concentration of hidrogen in the external phase
C_c	- Concentration of metal complex at the external-membrane interface (mol/l).
C_B	- Concentration of metal complex at the external-membrane interface (mol/l).
cP	- Centipoice
D	- Distribution coefficient
D_{32}	- Sauter mean diameter
D_{BM}	- Diffusion coefficient
D_{ec}	- effective diffusivity of solute-carrier complex in emulsion phase (m^2/s)

D_{eB}	- effective diffusivity of carrier in emulsion phase (m^2/s)
d	- Length of small cubic in cubic element (m)
E	- Recovery efficiency
ELM	- Emulsion Liquid Membrane
H	- Hidrogen ion
HR	- Carrier in organic phase
k_r and k_f	- Proportionality constant
K_E	- Equilibrium constants
K	- Temperature (Kelvin)
k_c	- Mass transfer coefficient through pheripheral layer of membrane (m^2/s).
k_B	- mass transfer coefficients of B in the peripheral thin oil
k_C	- mass transfer coefficients of C in the peripheral thin oil
M_B	- Rate of leakage
ppm	- Part per million
pH_{eq}	- pH equilibrium
P_o	- Permeation coefficient
R	- Sauter mean radius of an emulsion globules (m)
%R	- Recovery percentage
rpm	- Rotation per minute
R	- Radius
R_i	- Radius of emulsion globule
R_μ	- Radius of emulsion droplets
r_s	- rate of stripping

S' - sphere area of emulsion droplets

%S - Stripping percentage

S - Separation factor

S_A - Sphere area of globules emulsion

t - time (second)

v_f - Velocity of forward reaction

v_r - Velocity of reverse reaction

V_m - Volume of emulsion

V_{ext} - Volume of external phase

V_{int} - Volume of internal phase

V_{org} - Volume of membrane phase

$V_{int,f}$ - Final volume of internal phase

$V_{int,o}$ - Initial volume of internal phase

V_{III} - Volume of feed phase

V_I - Volume of membrane phase

V_{II} - Volume of internal phase

V_i - Volume of internal phase

V_i^o - Initial volume of internal phase

V_{III} - Volume of external phase (ml)

w/v - Weight per volume

$\eta_{s,ap}$ - Apparent swelling ratio

Greek letters

ϕ_1 - Ratio of internal volume to emulsion volume
β - Parameter for thickness of thin oil layer

δ - Thin oil layer

l - Length of cubic unit element (m)

∞ - Infinity

μ - Viscosity

μ_B - Viscosity of the solvent

ρ - Density

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

In the near future, the production of hazardous waste from industries will become a serious problem all over the world. These resources including inorganic solids or sludge containing metal were generated by many types of industries such as metal finishing, electronic, electrical, electroplating, machinery and other chemical industries. The amount of the nonferrous metal waste including minor components from municipal waste are reported to be about 2.0 million tons annually (Brooks, 1991).

The sources of metal wastes are diverse in nature and in its geographical distribution. The volumes of all kinds of wastes generated on the nationwide scale are formidable. In 1984, a national survey under U.S. Resource Conservation and Recovery Act reported that more than 264 million tons of hazardous wastes were generated by approximately 14,000 generators (Brooks, 1991). One of the hazardous waste generators is photographic industry which includes the manufacturing process, graphic arts, engineering and medicine. In Malaysia out of 417,413 MT total wastes generated in 1994, photographic waste accounted for 843.8 MT per year (Saidi and Ariffin, 1994). Beside silver the waste generated also contain other heavy metals like iron, zinc, lead, copper, nickel and chromium. Mainly silver existed in these waste as insoluble halide, soluble silver thiosulfate complex, silver ion or elemental silver depending on the type and the stage of the process.

One way to reduce environmental impact is through recovery of the valuable metals from industrial waste effluents. Therefore more efficient techniques for the recovery process are required. In principal the incentives for recovery are reduction in the volume and toxicity of the waste effluents, recovery of valuable metals and reduction of disposal costs. Furthermore, if these wastes were directly discharge into the natural water system, they will undoubtedly cause a lot of environmental problems.

Commercially, nonferrous metal that are significant to recycle as scrap are aluminum, copper and copper-base alloys, chromium, cobalt, cadmium, nickel, manganese, molybdenum, lead, titanium, zinc and other precious metals. According to statistics of recovery from U. S. Bureau of Mines Mineral Commodity Summaries in 1991 for 22 metals, recycling precious metals (except silver) ranges from 70 to 80 % but silver accounts for only 40 % (Brooks, 1991).

1.2 Research Background

Recovery of silver from photographic wastes is interesting because of the economic value of silver and also from environmental point of view. In photographic industry, silver is recovered from development and fixing solution, spent rinse water and scrap films. There are many methods which have been established commercially to recover silver from photographic wastes; these are precipitation, electrolysis, ion-exchange, and reductive exchange. Electrolysis is a commonly used method to recover silver from photographic wastes but it is not suitable for dilute silver concentration (less than 100 ppm) because the plating efficiencies are very low. This process requires high initial capital investment and high operating cost, and critical operating conditions that need to be constantly supervised. The 100 ppm of silver concentration in effluent is relatively high compared to recommended allowable discharge level of 0.1 to 1.0 mg/dm^3, which means that further treatment is required before it can be discharged to water stream.

The oldest and conventional method of silver recovery, precipitation, could not achieve the recommended discharge level although it has provided an effective technique for silver recovery. This is because an industrial effluent contains complexing agents which might bind to the silver metal. This metal complex is sometime very stable and not able to be precipitated by precipitation process. To overcome the problem many researchers found that emulsion liquid membrane extraction has a great potential and has been reported as an advanced technique for separating and concentrating metals. This separation technique has been tested in hydrometallurgy and wastewater treatment. Several pilot plants for recovery of zinc, copper, chromium, and nickel have proved the technical feasibility of the emulsion liquid membrane process (Reis and Carvalho, 1993).

In principal, the emulsion liquid membrane processes are a three phase dispersion system, where primary emulsion consist of organic and stripping phase is dispersed in the feed or effluent phase, which is the phase to be treated. For the separation of metals even in very low concentration, the carrier is an organic soluble extractant, which selectively combines with the solutes to form a metal-carrier complex. This complex will permeate through the membranes from the outer to the inner interface. At the inner interface, the complex decomposes by the reversal of the equilibrium reaction and the metal ion is liberated into the internal phase and the regenerated carrier goes back into the membrane phase. The advantages of this process compared to solvent extraction are extraction and stripping occurred simultaneously in one single step operation and equilibrium limitation can be removed. It also can reduce the amount of expensive extractant about 10 times (Fan, 1999), high fluxes and high selectivity are possible. Emulsion liquid membrane is also up to 40% less expensive than solvent extraction process (Noble and Way, 1987).

1.3 Research Objectives and Scopes

The main purpose of this study is to determine the possibility of developing the emulsion liquid membrane system for silver extraction from photographic waste. In order to successfully design and apply the system a good understanding of the system is very crucial and needs to be study in order to enlighten the fundamental understanding of the process as well as to develop a method that is capable of recovering silver selectively from photographic waste especially at dilute condition. The studies include the liquid membrane component selection, emulsion liquid membrane extraction performance and liquid membrane extraction model development.

First, the study focused on the selection of liquid membrane components, where experiments were carried out with different types of carrier and concentrations and the amount of metal extracted were recorded, while the other parameters were fixed. This screening process will identify a suitable carrier of silver and determine its selectivity in extraction process. According to the chemical reactions involved, these carriers were divided into four classes, namely acidic extractants like D2EHPA, Cyanex 272 and Cyanex 302; chelating extractants like 8-hydroxy Chinolin, dithizone, and tetramethylthiuram disulfide; basic extractants like TOA, Adogen 363, and TOMAC; solvation like TBP, Cyanex 471X, and TOPO. The carrier was reacted with metal to form a metal complex and diffused through the liquid membrane. On the other hand, these complexes must release the metal into the stripping solution easily. Several types of stripping solution were tested such as nitric, hydrochloric, and sulfuric acids, thiourea solution and sodium thiosulfate. Because extraction and stripping process occurred simultaneously in emulsion liquid membrane process, the best carrier and strip agent chosen must satisfy the reaction at external and internal interface of liquid membrane. After the selection of the carrier and strip agent, emulsion liquid membrane system was constructed. There are three components of emulsion liquid membrane; internal phase (stripping solution), external phase (feed phase) and membrane phase (consist of carrier, diluent and surfactant).

In emulsion liquid membrane, the type of emulsifier/surfactant and its concentrations strongly affect the rate of extraction and emulsion stability. The stability of the emulsion and the demulsification rate are very important factors in the extraction process and recovery of metal. Another factor is swelling rate that is controlled by the choice of surfactant and diluent. Swelling occurs when feed stream gets into internal phase by either osmotic pressure or physical breakage and subsequent reformation of the membranes. It will reduce the stripping reagent concentration in the internal phase which in turn lowers its stripping efficiency. However, in this study only SPAN 80 was used as emulsifier and type of diluents such as kerosene, n-dodecane, and toluene were chosen as a diluent in minimizing the co-transport of water and also depends of solubility of the carrier. All of these subjects were studied in the first objective.

In order to get a better understanding of emulsion liquid membrane process, the system potentials and extraction performance were studied based on the kinetics and thermodynamic aspects. The parameters that affect the silver extractability and selectivity were identified in the second objective. The parameters such as strip agent types and acidity that control the mass transfer of solute, volume ratio of emulsion to external phase that affect the mass transfer area of extraction process; carrier concentration, type of diluents, swelling, residence time and agitation rate that control the extraction performance and the break-up rate of emulsion were studied in this research. In order to obtain the optimum conditions in extraction of emulsion liquid membrane, one variable is changed whilst the other conditions remain constant. A high voltage demulsifier was constructed for emulsion breaking. All the parameters observed were carried out in batch system.

Finally, emulsion liquid membrane extraction model was developed based on permeation models developed by Kataoka *et al*. (1989), Lee *et al*. (1996) and Reis and Carvalho (2004) with some modification. An immobilized hollow spherical globule model approach is applied to the extraction process of silver ion through the ELM system. In order to satisfy the experimental finding some assumption were made based on the parameters that affect the emulsion liquid membrane extraction. Several external consideration such as emulsions distribution, uniformity of emulsion size and boundary conditions were also assumed Finally, this model was verified to perform the validity and stability of model based on existing models.

1.4 Report Outline

This report contains seven chapters. In the first chapter a brief description of the research backgrounds, research scopes and objectives were presented. Chapter 2 present the literature review about photographic waste and its characteristics, liquid membrane types and its prospect for silver recovery. In this chapter a brief description on liquid membrane component selection, parameters affecting emulsion liquid membrane process and also its theoretical models are discussed. Then, in Chapter 3, the research methodology including selection of liquid membrane components, emulsion liquid membrane extraction, emulsion demulsification and analytical procedures were reported. Afterwards, the results and discussions of liquid membrane component selection and emulsion stability were discussed in Chapter 4 followed by Chapter 5, explaining the main advantage of emulsion liquid membrane in extraction of silver from photographic waste. In this chapter, several parameters affecting the silver extraction and recovery, breakage and swelling phenomena during the ELM process were discussed in detail. In Chapter 6, an emulsion liquid membrane extraction model was developed from the experimental data obtained. Numerical solution using line procedure method was used to predict the simulation results.

Chapter 7 stated of the general conclusion and directions for future work.

1.5 Summary

Metal extraction with emulsion liquid membrane process is attractive due to its high selectivity and could be used for dilute metals system compared to conventional solvent extraction process. This process is technically favorable because of low energy consumption is and organic liquid losses are often negligible.

The choice of carrier and strip agent is vital for the success of the process and the choice is based on the conventional liquid-liquid extraction studies. High extraction efficiency and achievement of optimal system performance will be realized if the liquid membrane system and operating parameters are properly chosen. Parameters that influence the performance of emulsion liquid membrane extraction process will be studied experimentally and theoretically.

CHAPTER 2

LITERATURE STUDY

2.1 The Photographic Industry

Photograph is a permanent record of an image on a light sensitive surface. The surface is usually a transparent film covered with a layer of silver halide in gelatin. The most commonly used silver halides in photographic industry are silver chloride, silver bromide and silver iodide but normally silver iodide is used as a mixture with silver bromide (Smith and Bonnie, 1977).

There are three stages of manufacturing photographic material, which include emulsions making, emulsion supports or film and the last stage is film coating. In making of emulsions, silver halide crystals are formed in the desired size and the soluble salt are removed by washing then the emulsion is digested in the presence of special agents. The support of emulsion must meet high standards of physical properties including high transparency, high rapture and tearing strength, freedom from curl, stiffness, elasticity, good dimensional stability, and low coefficient of friction. Commonly the supports used are papers with barium sulfate or polyethylene coating and plastic films (cellulose triacetate or polyester). The last stages is coating on the emulsion support. This coat consists of light-sensitive layers and a number of auxiliary layers to perform the following functions: light filtration separation of differently sensitized emulsions containing different dye couplers, antihalation, mechanical protection, noncurl, subbing, antistatic and others. In addition the gelatin-based emulsion layer must also adhere well to the support during every stage of use and processing (Keller, 1993).

Four steps are involved in a complete photographic processing; exposure of film to light in order to produce a latent image, image development to produce a negative, permanent image making or fixing process and the last step is positive print-out from negative. During the development stage, a silver image and a dye image are formed in each of emulsion layer. In production of colour image, this silver must be bleached (oxidized) using oxidizing agents such as the iron (III) – EDTA complex, hexacyanoferrate (III), or potassium peroxodisulfide along with a thiosulfate as complexing agent without disturbing the image dye. In fixing step, white couplers (suitably substituted pyrazolones) will react with developer oxidation products to form colourless products, before these oxidation products can combine with the couplers in the emulsion to form non-image dyes.

The production of silver from photographic processing is chiefly from fixing baths, and secondarily from bleaching baths and rinse water. Figure 2.1 shows the flow diagram of colour negative process.

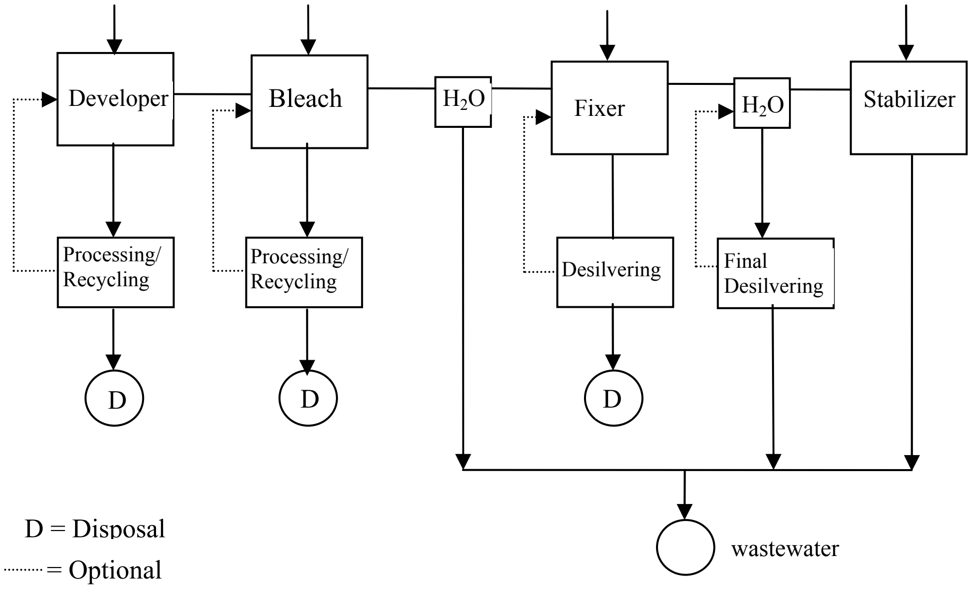


Figure 2.1: Photo colour negative process (Baumann and Grafen, 2001).

2.1.1 Silver in Photographic Processing

Silver used in photographic processing is a naturally occurring element and a precious metal. Silver is unique in its ability to react to light and produce images in applications such as photography and radiography. No other metallic element possesses these properties. However, silver is classified as an environmentally hazardous heavy metal in all countries. Silver ion is highly toxic to bacteria and fish especially free silver ions. Free silver ion occurs in photographic industry only in emulsion making but not in the downstream production steps, in the photographic materials or in the processing baths. Waste from photographic processing especially fixing waste usually contains silver hydroxide complex and silver chloride associated with suspended particles or present as thiosulfate complexes, thiocyanate, colloidal silver chloride and sulfide, ferrocyanides, acetate, halides, ammonium and soluble complex. Silver released from photographic processing are primarily from fixing baths and secondly from bleaching baths and rinse water (Keller, 1993). During these stages, silver is removed from the film or paper usually in the form of silver thiosulfate complex. As much as 80% of the total silver processed for black and white positives and almost 100% of the silver processed in colour work will end up in the fixer solution (DEHNR, 2001). If wastes were directly discharged into the natural water system, they will undoubtedly cause a lot of environmental problems. Table 2.1 shows the aquatic toxicities of the silver thiosulfate complex, silver sulfide and silver chloride relative to the free silver ion. Thus, the silver thiosulfate complex represents the usual soluble form of silver to be recovered and in the molar ratio of thiosulfate(Th)/Ag greater than 1.0 the system is soluble, making it virtually impossible for free silver ions to exist in any significant concentration in such environments (Zouboulis, 1995). However, strict limitations on the discharge of aqueous silver effluents have been concerned with the total amount of silver, with no regard to the form in which it occurs.

Table 2.1: Relative toxicity of silver compounds in comparison to free silver ion (Keller, 1993).

Substance	Relative toxicity
Ag^+	1
AgCl	0.003
Ag_2S	$< 0.7 \times 10^{-4}$
Ag-thiosulfate	$< 0.6 \times 10^{-4}$

2.1.2 Silver Recovery Technology

There are several reasons to be interested in the recovery of silver from photographic wastes. Silver is a valuable natural resource of finite supply, it has monetary value as a recovered commodity, and its discharge to the environment is very strictly regulated. It is estimated that about 12% of the world's silver resources are used in the production of light-sensitive materials like photographic industries. On the other hand, all over the world several tens of tons of silver are lost annually from photographic and galvanizing plants. The wastes containing organic and inorganic compounds are usually sent for electrolytic silver recovery in the processing plant itself. However, small-scale industries like photographic shops do not have enough capital to set up their own treatment system. Usually, they sell it to a recovery firm for various prices depending on the characteristic of the waste.

There are many methods which have been established commercially to recover silver from industrial wastes. Several authors, using a variety of hydrometallurgy procedures, as well as equipment types and sizes, have investigated silver recovery from dilute solution, applying different techniques, each having specific advantages and disadvantages. As a result, several technologies have been found for silver recovery such as precipitation, ion exchange, electrolytic process, metallic replacement, and membrane separation. Other methods for the removal of silver are adsorption, ozonation, physicochemical or biological treatment (Zouboulis, 1995). However, it should be stressed that the choice of specific technique employed will ultimately depend on such factors as environmental and ecological processes, the price of silver, the operating and capital cost for its recovery, practical operational considerations and experience with a particular removal system. The following section will discuss in detail about the process due to it transfer mechanism and its potential. Table 2.2 highlights some advantages and disadvantages of several methods used in silver recovery process.

Electrolytic recovery is regarded as the best method for the big processors of photographic waste solutions but most of the wastes are not sufficiently concentrated for electrolytic recovery. This method requires high initial capital investment and high operating cost since the critical operating conditions must be constantly supervised. As reported by Smith and Bonnie (1977), this method had an ability to recover up to 96% purity of silver. Combining electrolytic silver recovery with in-situ ion exchanges can result in more than 99.5% silver recovery efficiency (DEHNR, 2001). In the electrolysis process, a controlled direct electrical current is passed between two electrode suspended in the silver-bearing solution. Silver is deposited on the cathode. The cathode is removed periodically and the silver is stripped off for sale or reuse. This method also requires additional chemicals to compensate for dilution by carryover. Therefore there is some increase in volume to be discarded eventually. Beside this, sulfide is lost by oxidation at the anode and must be replaced. If the electrolytic recovery is continued for long time, silver sulfide may be formed at the cathode or in solution, so it may be necessary to discard some or all of the fixer to prevent dirt problem on the process product (Cooley and Vacco, 1993). Smith and Bonnie (1977) and Bhavani *et al.* (1994) reported that this process needs a lot of capital investment for commercialized industrial practice and use a large amount of electricity during the electrolysis process.

Table 2.2: Silver recovery methods (Goshima *et al.*, 1994).

Method	Advantages	Disadvantages
Metallic replacement	- Low investment. - Low operating cost.	- Effluent contains high iron. - Silver recovered as sludge. - Effluent has high silver content unless 2 units are used in series.
Electrolytic recovery	- Silver recovered as pure metal. - High silver recovery.	- Sulfide formation possible. - Effluent has high silver content.
Precipitation	- Can attain 0.1 mg silver/liter. - Low investment.	- Complex to operate. - Silver recovered as sludge. - Treated solution cannot be reused. - Potential hydrogen sulfide released.
Reverse Osmosis	- Also recovers other chemicals. - Purified water is recyclable.	- Concentration requires further processing. - High investment. - High operating cost.
Ion exchange	- Can recover 0.1 to 0.2 mg silver/liter.	- Only for diluted solutions. - Complex operation. - High investment.

The oldest method of silver recovery is precipitating silver by using sulfide ions but for large-scale the use of sulfide precipitation leads to problems with respect to solids separation and handling. In order to solve the problems, treatment with hydrosulfite ion $(S_2O_4)^{2-}$ yields Ag and Ag_2S as compact and settle able precipitates. However, the process required heat and has high chemical costs (Sittig, 1973). Chemical methods for precipitating silver from motion-picture photographic waste solutions require an addition of sodium sulfide. The result was dry sludge containing 40 to 70 % of silver. By adding sodium hydrosulfite ($Na_2S_2O_4$), the sludge contains 85 % Ag as Ag and Ag_2S. Precipitation of silver could be also carried out by adding magnesium sulfate or calcium hydroxide, hydrolyzed sugar solution, sodium hydroxide, or exhausted developer or boiling to precipitate silver sulfide. Sittig (1973) reported that the addition of magnesium sulfate and lime could be carried out to precipitate the silver from the photographic waste solutions as a mixed sulfate-oxide. The silver was then recovered from the sludge. In this method, solution that contain silver thiosulfate complex, such as exhausted thiosulfate fixing solutions, were chlorinated with Cl_2 or NaOCl under alkaline conditions to precipitate a silver-bearing sludge from which silver could be separated.

Ion exchange process has received considerable attention for separation and concentration of a variety of metals from waste effluents. It is generally used for effective recovery of silver from rinse water or other dilute solutions of silver. The ion exchange method involves the exchange of ions in the solution with ions of similar charge on the resin. The soluble silver thiosulfate complex is exchanged with the anion on the resin. This is the exhaustion step and is accomplished by running the solution through a column containing the resin. For large operation, the next step is the regeneration step in which the silver is removed from the resin column with a silver complexing agent such as ammonium thiosulphate. This method are considered uneconomical for silver recovery from photographic waste but are feasible for low silver concentration in separating waste streams where the total ionic strength is not much greater than the silver salt concentration (Smith and Bonnie, 1977). In consequence, ion exchange equipment more resembles a manufacturing plant than a waste water treatment facility. As a result, ion exchange has been regarded more as a method to produce pure water than as a method to purify waste (Heikki, 1999).

Another type of silver recovery technology is metallic replacement (reductive exchange) process. This technology uses equipment commonly referred to as Chemical Recovery Cartridges, Metal Replacement Cartridges or Passive Silver Cells (PRO-ACT, 1995). This technology is simple in principle and operation and it consist of a cartridge filled with steel wool or iron particles connected to the fixer or rinse bath overflow and the excess solution flows through the unit under gravity. Metallic replacement involves precipitation of silver onto another metal, usually zinc or iron, which releases zinc or iron ions in solution. This method is employed using a less noble metal than silver and is allowed to come into contact with the exhausted fixer. The silver is deposited as sludge or as a coating, depending upon the physical form of the metal used and the metal ions pass into the hypo-solution ($Na_2S_2O_3$). This method is not suitable for extensive re-use of the fixer but has been recommended for use by small photographic developing plants. The Bureau of Mines developed a process that employed steel wool or steel window screen and a smelting process to recover pure silver from sludge containing 27 to 80% silver (Smith and Bonnie, 1977). If this technology was used properly, it can reduce silver concentration to below 1 ppm in the effluent at a low cost (PRO-ACT, 1995).

A common method of metals extraction that has been extensively used in hydrometallurgical operations and more recently in the treatment of wastewaters to remove soluble metals is solvent extraction. Because salts are usually not soluble in organic solvents, the process requires the introduction of an extractant that will combine with the metal ion to form an organic soluble species. The loaded solvent is then mixed with a suitable aqueous phase, and the metal is transferred from the organic to the aqueous solution or stripping phase. Most of the general types of compound available as extractants are dicarboxylic acids, aliphatic amines, aromatic amines, amino acids, and hydroxyl acids. The biggest disadvantage of solvent extraction compared with liquid membrane process is that it must always be in equilibrium conditions. In addition the selectivity of this separation is quite dependent on pH and maximum advantage must be taken of this parameter in combination with the type of extraction agent chosen (Preston, 1985).

A new promising technology of metal recovery is membrane separation. There are several types of membrane process used for metal separation such as reverse osmosis, electrodialysis, ultrafiltration, and several kinds of special liquid membranes namely emulsion liquid membrane and immobilized liquid membrane. In electrodialysis cell there are ionic membranes adjacent to the electrodes, anionically charged (sulfonate exchange resin) for the anode and cationically charge (quaternary ammonium resin) for the cathode. In reverse osmosis, the pressure pushes water through a semi-permeable membrane to concentrate the charged metal species. Ultrafiltration achieves separation based on the filtering effect of the membrane pores relative to the molecular size of solute species under imposed hydrostatic pressure (Lacey, 1972).

From the literature, membrane separations have been applied to ten metals such as Ag, Al, Cd, Co, Cr, Cu, Hg, Mn, Ni, and Zn (Brooks, 1991). The membrane separation process is most appropriate for dilute solutions such as rinse water. Most membranes are fragile mechanically and vulnerable to degradation by corrosive and strongly oxidative systems such as concentrated chromic acid. Separation efficiency also requires elimination of insoluble and suspended solids, which block the membrane surfaces except the liquid membrane process.

One type of special liquid membrane consists of interfacial surfactant films in emulsion is liquid surfactant membrane or emulsion liquid membrane (ELM). There are several advantages compared to solvent extraction process. However the concepts of transfer mechanism are the same. Some of these advantages are simultaneous extraction and stripping process, features that the equilibrium limitation will removed, reduction of amount extractant used, selective separations and high fluxes are possible, and reported less expensive than solvent extraction (Noble and Way, 1987). With these advantages the liquid membrane process becomes an attractive alternative and a promising technology to apply in research and industry.

2.2 Liquid Membrane Technology

2.2.1 Introduction

Liquid membrane technology is introduced and is identified as a subset of membrane science. This technology has attracted increasing attention for its potential capability in the field of separation and has been demonstrated as an effective tool in many applications. Some review papers on liquid membrane and facilitated transport have appeared in the literature. Smith *et al*. (1977) summarized experimental and theoretical work since 1974 on the facilitated transport, Kimura *et al*. (1979) discussed potential industrial applications of facilitated transport membranes, Goddard (1977) discussed the application of facilitated transport under reaction equilibrium conditions and Halwachs and Schugerl (1980) presented a general discussion of liquid membranes and describe some possible industrial applications. Douglas *et al*. (1982) surveyed and reviewed the potential of immobilized liquid membrane and emulsion liquid membrane, its transport mechanisms and also mathematical modeling and analytical solutions. Several kinds of liquid membranes have been used in various disciplines, such as chemical engineering, inorganic chemistry, analytical chemistry, physiology, biotechnology, and biomedical engineering. Within these disciplines, the method has been applied to a wide variety of uses, such as gas separation, organic compound removal, metal ion recovery, pollutant removal and bio-separation. The technology is particularly attractive when very dilute solutions are involved since the treating ratio between receiving phase and source phase can be drastically reduced.

Liquid membrane extraction is a three-phase process; two of these are miscible with each other but separated by the third phase which is the membrane phase. This membrane can be supported or emulsified and it immiscible with the other two. Solute extraction is achieved by mass transfer between the two miscible phases through the membrane phase. For water/oil/water system, it is the immiscible oil phase separating the two aqueous phases.

2.2.2 Liquid Membrane Process

In liquid, different solutes have different solubility and diffusion coefficients. The product of these two terms is a measure of the permeability. A liquid can yield selective permeability and therefore separation occurred. Because the diffusion coefficients in liquids are typically orders of magnitude higher than in polymers, a larger flux can be obtained.

Liquid membranes can be prepared in two different configurations. A liquid can be impregnated in the pores of a porous solid for mechanical support. This form is commonly known as an immobilized liquid membrane (ILM). In the alternate configuration, the receiving phase is emulsified in an immiscible liquid membrane. This type of liquid membrane is known as a liquid surfactant or emulsion liquid membrane (ELM). Liquid membranes also can be performed in two modes, with or without a chemical carrier. With a chemical carrier, diffusion of permeate species is increased by diffusion of the reaction product. In process without an active carrier, the liquid membrane relies on solubility differences and /or diffusion coefficient differences to separate components. This will be discussed more in related section.

In emulsion liquid membrane application, the emulsion must be demulsified into two immiscible phases after the extraction step of the process. This is accomplished by heating, application of electric field, or centrifugation. The liquid membrane phase containing the surfactant and carrier will be recycled to the emulsion preparation step while the internal phase of the emulsion containing the concentrated solute will undergo further purification in the recovery process or treatment and disposal in the purification process. The metal extraction process using emulsion liquid membrane extraction process is shown in Figure 2.2.

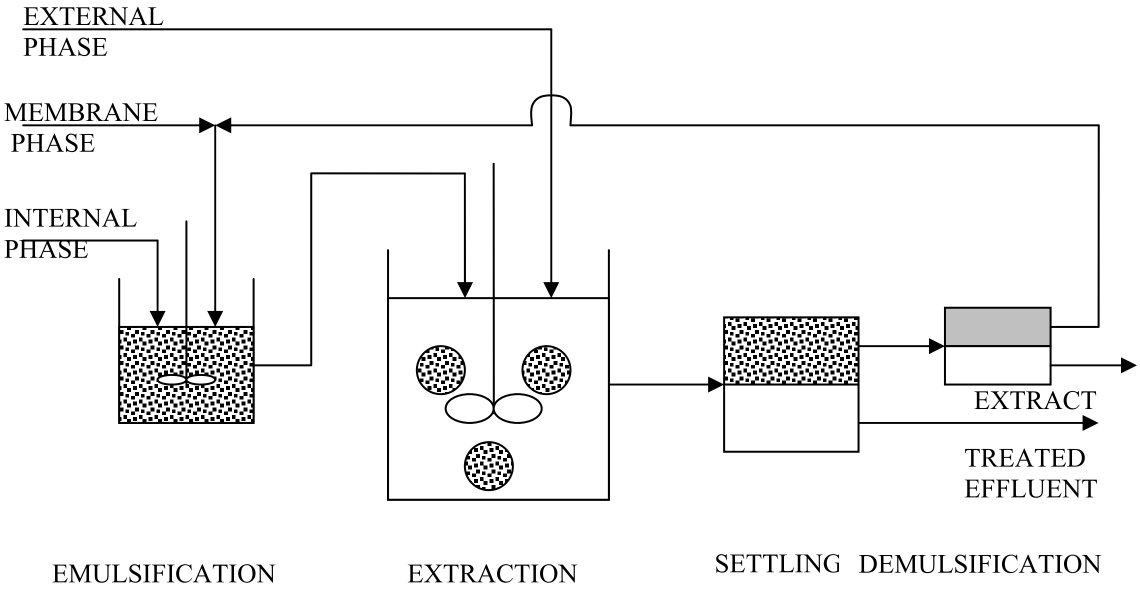


Figure 2.2: A schematic diagram of mixer-settler extraction using in emulsion liquid membrane (Jiang *et al*., 2001).

2.2.3 Liquid Membrane Formulation

2.2.3.1 Carrier

A carrier or extractant is a reagent, which forms a complex or other adducts in the solvent with the substance which partitions across the phase boundary of the extraction system (IUPAC, 1993). The carrier (extracting agent) may also partition between the phases involved (Rydberg *et al*., 1992). The following are the four benefits of using carrier in liquid membranes;

i) High fluxes are possible. By combining the advantages of high diffusion coefficients in liquids with added carrying capacity of the carrier, larger fluxes than in polymer membranes are possible.

ii) Very selective separations are possible. The selective nature of the carrier provides much better separations than those obtainable based solely on relative solubility and diffusion.

iii) Ions can be concentrated. Coupled transport allows one to pump ions against their concentration gradient.

iv) Expensive extractant can be used. Small amounts of carrier are used because of the small solvent inventory associated with the membrane and because of the nonvolatile nature of the carrier.

There are three types of carriers such as extractant involving compound formation, ion association and solvation. Extractants involving compound formation can be divided into acidic extractants and chelating extractants. Acidic extractants, or cation liquid ion exchangers, extract metals by cation-exchange mechanism, in which hydrogen of the extractant are exchanged for metal ions. The acidic type extractants, which have been found useful as metal extractants in commercial operations are organic derivatives of phosphorus acids and monocaboxylic acids. This group includes esters of orthophosphoric, phosphonic and phosphinic acids, and similar compounds containing polyfunctional groups. The active group of these organophosphorus acids is >P (O) OH which is responsible for their extractive properties. Another extractant are SME 418 and PC-88A, which is an ester of a phosphonic acid developed by shell and Daihachi, Chemical (Ritcey and Ashbrook, 1984). Cyanex 272 is a further development in the alkyl phosphorus reagents. This is a phosphinic acid extractant. It will extract many metals, depending upon the equilibrium pH. In these reagent sulfate and carbonate ions form more stable metal-anion complexes in the aqueous phase than do nitrate ions.

On the other hand, chelating extractants contain donor groups capable of forming bidentate complexes with metal ions (Baird and Hanson, 1983). In the majority of chelating extractive system it was observed that whenever the coordination number of the metal doubles its ionic charge, the chelate formed satisfies the coordination requirements of the metal and the metal is readily extractable into both polar and non-polar solvent.

Commercially available chelating extractants are limited to two types; LIX and KELEX (Ritcey and Ashbrook, 1984). The other extractant are SME and Acorga. The first commercially available is LIX chelating extractant designed specifically for the selective extraction of copper (Dalton and Price, 1982).

Consequently, in commercial solvent extraction processing, basic extractants are limited to amines and quaternary halides, primary (RNH_2), secondary (R_2NH), tertiary (R_3N) amines and quaternary ammonium salts $(R_4N)^+$. Rydberg *et al.* (1992) reported that the usefulness of amines as extractants is usually considered to depend essentially on the ability of metal ions to form anionic species in the aqueous phase, which are extracted by amines in an anion-exchange process. Extraction metal M^{n+} by an amine salt $R_3N.HA$ can be represented as an anion exchange process such as:

$$MA_m^{(m-n)-} + \overline{(m-n)(R_3N.HA)} \leftrightarrow \overline{(R_3N^+H)}_{m-n}MA_m^- + (m-n)A^- \qquad (2.1)$$

One important factor influencing the extraction of metals by amines is the aggregation of the amine in the organic phase, which is determined essentially by the nature of the diluent. Ritcey and Ashbrook (1984) reported that the ease of extraction of complex metal anionic species from chloride media by amines follows the order: quaternary > tertiary > secondary > primary. Other factors are the nature of the carbon chain and also the number of carbon atoms in the chain. Normally, aliphatic amines are the best extractants; aromatic substituents, especially when attached to the nitrogen atom.

The main problems associated with the use of amines as metal extractants are similar to those involving acidic extractants, namely salt effects, aggregation in the organic phase, third phase formation and solubility. Salt effect generally will decrease metal extraction by amines in the order of $ClO_4^- > NO_3^- > Cl^- > SO_4^- > F^-$.

The third type of extractant is solvating extractant. This extractant rely on the power of oxygen-containing organic extractants to solvate inorganic molecules or complexes. By such solvation the solubility of the inorganic species in the organic phase is greatly increased. There are two main groups of extractants: organic reagent containing oxygen bonded to carbon and oxygen or sulfur bonded to phosphorus. Extractants containing oxygen-carbon bond are useful primarily for the extraction of metal halide complexes but not for metal sulfates.

Extractant containing carbon-oxygen bonds are essentially ethers (C-O-C), esters (-COOR), alcohols (C-OH), and ketones (C=O). They are all electron donating reagent but alcohols, being amphoteric, exhibit both donor and acceptor properties and resemble water in many ways. Only one ketone appears to have been used commercially for the extraction of metals, namely MIBK (methyl isobutyl ketone) (Ritcey and Ashbrook, 1984).

Extractant containing phosphorus-oxygen bonds could be considered as the derivatives of phosphoric acid such as alkyl-phosphate esters (≡P=O). The extraction mechanism is mainly the same for all of them and it is the oxygen of the phosphoryl group that is responsible for the coordination bond formed with the metal. Extractive power of phosphorus-containing extractants increases with increase in the number of carbon-phosphorus bonds over the series: phosphate – phosphonate – phosphine oxide.

The most well known and most used of the organophosphorus esters is undoubtedly try-n-butyl phosphate (TBP). Generally at low acid concentration the solubility decreases so that increasing salt concentration in aqueous phase will decrease the solubility of TBP. For TBP, if the acid concentration is increased, the extraction of metal increases (Rydberg *et al.*, 1992).

Lastly is extractant containing phosphorus-sulfur bond which is corresponding to sulfur group such as alkylthiophosphoric, alkylthiophosphonic and alkylthiophosphinic acid esters as well as phosphine sulphides like tri-iso-butylphosphine sulphide (Cyanex 471X).

2.2.3.2 Diluents

The diluent is a liquid or homogeneous mixture of liquids in which extractants and possible modifier may be dissolved to form the solvent (IUPAC, 1993). The general requirements of the diluent are (Ritcey and Ashbrook, 1984):

- mutually soluble with an extractant
- have high solvency for an extracted metal species, thus minimizing both the problem of third phase formation and low loading capacity of a solvent
- have low volatility and high flash point, thus decreasing losses due to volatility as well as fire hazards
- insoluble in the aqueous phase
- have a low surface tension
- cheap and readily available

Several properties need to be considered in selecting the suitable diluents. These include properties such as specific gravity, viscosity, flash point and polar nature. The most common diluents used are n-hexane, kerosene, cyclohexane, benzene, toluene, carbon tetrachloride, and chloroform. Aliphatic diluents are generally preferred compared to aromatic diluents. The physical properties for these low polarity diluents are shown in Table 2.3.

In general, the aromatic products have specific gravities higher than the aliphatic products, which could inhibit dispersion and coalescence properties of a solvent containing them. At high metal loading of the solvent, the difference in specific gravity of the loaded solvent and aqueous phase could be small, which might present problems in separating the two phases. The density of the solvent usually increases as the concentration of extractant is increased, thus the density of the diluent becomes a factor to be considered (Ritcey and Ashbrook, 1984).

Table 2.3: Physical properties of various diluents (Sekine and Hesegawa, 1977; Rydberg *et al*., 1992).

Diluents	Chemical formula	Molecular weight (gmol)	Density (g/mL)	Viscosity (cP)	Dielectric constant
n-hexane	C_6H_{14}	86.17	0.65937	0.23	1.88
Kerosene	-	-	0.80	0.02	2.0 – 2.2
Cyclohexane	C_6H_{12}	84.16	0.77855	0.98	2.02
Benzene	C_6H_6	78.11	0.87903	0.65	2.28
Toluene	C_7H_8	92.13	0.86694	0.59	2.24
Carbon tetrachloride	CCl_4	153.82	0.965	0.97	2.24
Chloroform	$CHCl_3$	119.38	1.563	0.57	4.81

On the other hand, metal loading affects the viscosity of the solvent. The viscosity increases with increasing metal loading. It becomes necessary to operate the solvent extraction system at elevated temperature both to reduce viscosity effects and to increase the rate of separation of the phases. In considering the suitability of the diluents the solubility in the aqueous solution and the flash point are important. The very low flash point-diluent causes environmental problem because it will easily flash at low temperature operation. Thus, it is advisable to use diluents having much higher flash point.

The more important factor is the polarity of the diluents. The extractions of metals decrease with an increase in the polarity of the diluent. Interaction of the diluent with the extractant can result in lower extraction coefficient for metal ions. Therefore the diluents with lower dielectric constant were suggested for the highest extraction.

2.2.3.3 Emulsifier/Surfactant

Emulsifier or surface-active agent is a substance that, when present at low concentration in a system, has the property to adsorb onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surface or interfaces. The interfacial free energy is the minimum amount of work required to create that interface. Due to changes in the amount of work required to expand those interfaces, surfactants usually act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it.

Surfactant have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group and a group that has strong attraction for the solvent, called the lyophilic group. This is known as an amphipothic structure. When surfactant is dissolved in a solvent, the presence of the lyophilic (hydrophobic) group in the interior of the solvent causes a distortion of the solvent liquid structure and increasing the free energy of the system. That means less work is needed to bring surfactant molecule to the surface. On the other hand, the present of hydrophilic group prevents the surfactant from being expelled completely from the solvent as separate phase, since that would require desolvation of the hydrophilic group. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the solvent, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it as shown in Figure 2.3. Hydrophilic groups may be cationic (organic amines, especially with three hydrocarbon chains attached to the nitrogen atom), anionic (fatty acids or sulfates with hydrocarbon chains) or nonionic (organic compounds with oxygen containing groups such as alcohols, esters and ethers). Lipophilic groups may be large, straight or branched chain hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons and or combination of them (Lin, 2001).

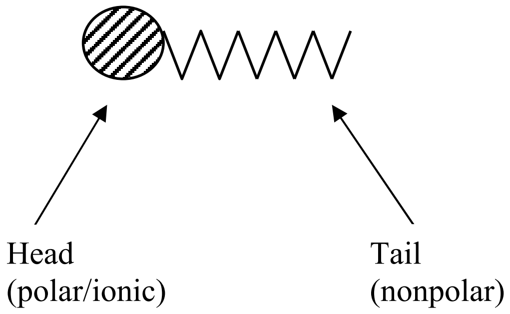


Figure 2.3: The structure of surfactant.

Surfactants are characterized according to the balance between the hydrophilic and lipophilic portions of their molecules. The hydrophilic-lipophilic balance (HLB) number indicates the polarity of the molecules in an arbitrary range of 1-40, with the most commonly used emulsifiers having a value between 1 and 20. The HLB number increases with increasing hydrophilicity. According to the HLB number, surfactants with HLB values in the range 3-6 promote W/O emulsions while value between 8 and 18 promote O/W emulsions. Since the primary emulsion in this research is W/O emulsion, therefore it is important to select the surfactant within the range of 3-6.

Span 80, also known as sorbitan monooleate, is a nonionic surfactant with a HLB value of 4.3 and a molecular weight of 428 (Figure 2.4). It is selected as the surfactant in this research because it is the most popular surfactants used in research (Table 2.4) and its selection obeys the HLB rules (Kargari *et al*., 2003). However, there are some disadvantages of Span 80 mainly its poor chemical stability and it undergoes hydrolysis reaction in moderate acidic and basic media (Kasaini *et al*., 1998). Besides, it is also a carrier of water molecules and it therefore changes several properties of the W/O emulsion and it could also be destroyed by bacteria (Kargari *et al*., 2003). Synthesizing a specialized surfactant which is more stable is another alternative in the selection of surfactant. However, the synthesis process takes time and it is not easily available in the market. Therefore, Span 80 becomes a more practical choice for this research purpose.

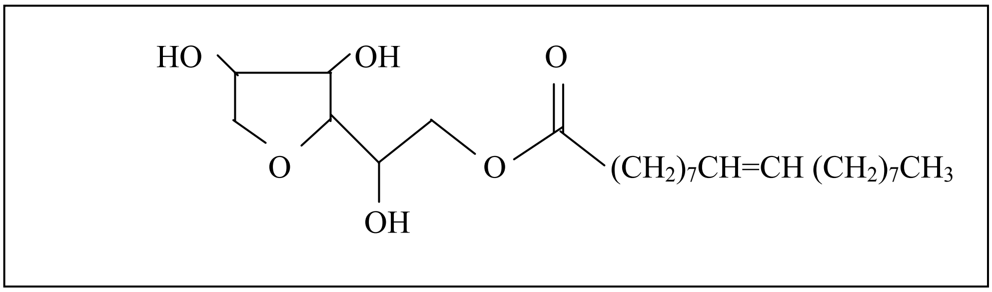


Figure 2.4: Molecular structure of Span 80.

As a summary, the following are the capabilities required of a suitable surfactant in emulsion liquid membrane;

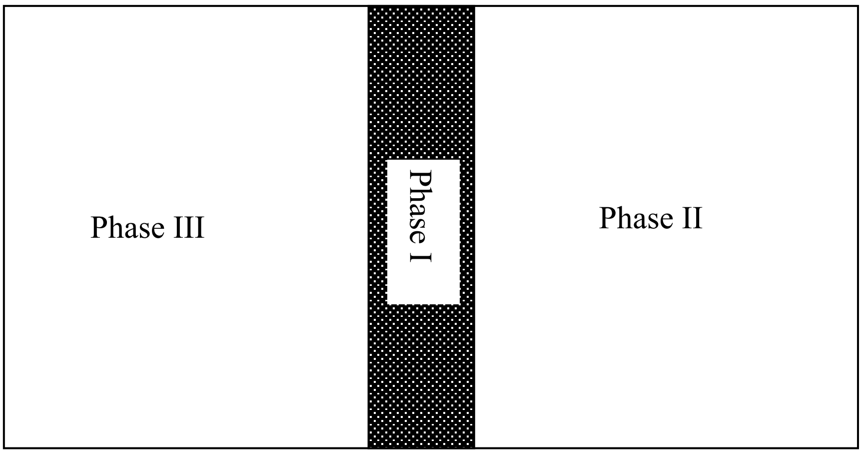
i) lowering of the break-up rate of the emulsion globules in a mixer
ii) lowering of the swelling rate of the emulsion globules due to osmotic pressure
iii) enhancement of the extraction rate of metal
iv) keeping high selectivity for the metal to be separated
v) ease of demulsification of the emulsion
vi) chemical stability and safety of the surfactant

2.2.4 Liquid Membrane Modes of Operation

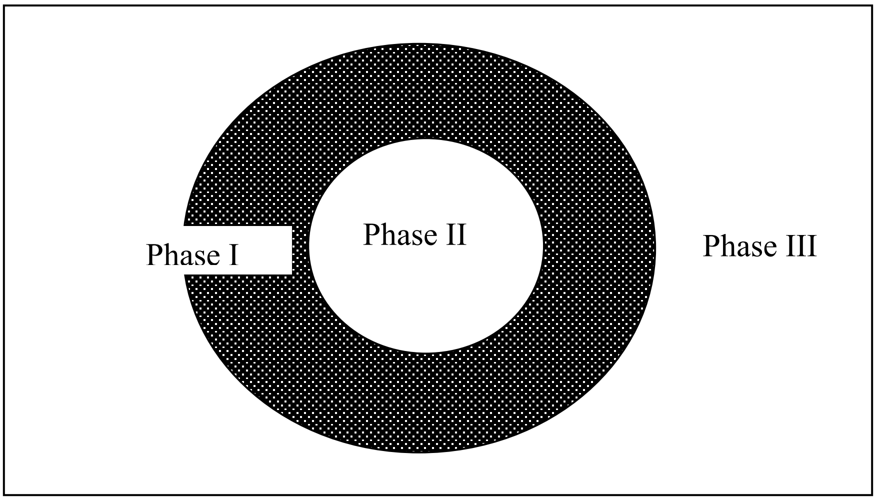
A membrane has been defined as an inter-phase between two phases. The inter-phase may be solid or liquid. In liquid membrane process, the liquid film will separates two phase from each other. The separation process occurs because of differences in solubility and diffusivity in the liquid film. There are two types of liquid membrane; Immobilized Liquid Membrane (ILM) or Supported Liquid Membrane (SLM) and Emulsion Liquid Membrane (ELM) or Liquid Surfactant Membranes (LSM) (Figure 2.5).

2.2.4.1 Immobilized Liquid Membrane (ILM) or Supported Liquid Membrane (SLM)

The liquid film is immobilized within the pores of porous membrane. The porous membrane serves only as framework or supporting layer for the liquid film. Such membrane can be easily prepared by impregnating a (hydrophobic) porous membrane with a suitable organic solvent.



(a) Immobilized Liquid Membrane



(b) Emulsion Liquid Membrane

Figure 2.5: A schematic diagram of two types of liquid membranes.

An ILM can be made in at least three different geometries. The first one is planar or flat geometry which is very useful for laboratory purposes and for industrial purposes. However a planar geometry is not very effective since the ratio of surface area to volume is too low. Therefore, hollow fiber and spiral wound modules can be used to provide high surface area to volume ratio, which approach 10000 m^2/m^3 for hollow fiber and 1000 m^2/m^3 for spiral wound modules (Lonsdale, 1982).

There are two primary problems associated with the use of immobilized liquid membrane, which are solvent and carrier loss. Solvent loss occurred because of evaporation, dissolution, or large pressure differences forcing solvent out of the pore support structure. Carrier lost is due to irreversible side reactions or solvent condensation on one side of the membrane. To overcome the problems, ion exchange membranes have recently been studied by many researchers.

2.2.4.2 Emulsion Liquid Membrane (ELM) or Surfactant Liquid Membrane.

Emulsion liquid membranes are known as double emulsions system. The primary emulsions were prepared by emulsifying two immiscible phases of the stripping solution and organic phase with a surfactant to produce an emulsion. This primary emulsion is then dispersed in the solution to be treated. Mass transfer takes place between the feed phase and the internal phase through the membrane phase.

For example, two immiscible phases, water and oil are mixed vigorously and emulsion droplets are formed, which are stabilized by the addition of surfactant. This emulsion (water/oil emulsion) is added to a large vessel containing an aqueous phase where a water/oil/water emulsion is now formed, the oil phase being the liquid membrane in this concept. The major problem associated with ELMs is emulsion stability. If the emulsion globules break and the inner droplet phase spill into the continuous phase the separation is lost. Interfacial shear between the continuous phase and membrane phase causes the liquid membrane to thin and in some cases, rapture.

Another problem is osmotic swelling although it is rarely mentioned in the literature. This phenomenon occurs when water in external phases diffuses through the organic membrane phase and swells the inner aqueous droplet phase. The increased volume of the internal phase leads to increased breakage and dilution of the concentrated droplet phase.

Under agitation the emulsion liquid membrane phase separates into spherical globules of emulsion, which have typical diameters of 10 μm to 1 mm. Each globule contains many droplets of encapsulated inner or receiving phase with a typical size of 1 to 10 μm in diameter. Therefore, emulsion will produce large surface area/volume ratios for very rapid mass transfer (Marr and Kopp, 1982).

The emulsion liquid membrane process consist of three important components, they are:

i) Internal phase (receiving phase): an aqueous phase, actually made up of encapsulated droplets, which will receive the solute.
ii) External phase (source phase or feed phase): a continuous aqueous phase of feed/waste water which is the source of the metal ions.
iii) Membrane phase: an organic phase that separates the internal droplets in the emulsion from the external phase. It usually consists of three components.
    a) Diluents/organic solvent
    b) Surfactant/stabilizer of the system
    c) Extractant/ carrier to transfers the metal ion from external to internal phase.

In order to make this system more promising, Kopp *et al.* (1978) created a set of guidelines for the formation of stable water in oil of emulsion liquid membranes:

i) Organic phase soluble surfactant concentration, 0.1 to 5 wt %;
ii) Organic phase viscosity, 30 to 1000 mPa.s

iii) Volume ratio of the internal receiving phase to membrane phase, 0.2 to 2.0;
iv) Volume ratio of internal phase to continuous external phase, 0.2 to 0.05;
v) Volume ratio of continuous phase to emulsion phase, 1 to 40;
vi) Surfactant HLB value, 6 to 8.

2.2.5 Mass Transfer Mechanism of Liquid Membrane Process

There are three types of mass transfer mechanism involved in liquid membrane system:

a) Diffusion only, without any reaction involved and being used in hydrocarbon applications.
b) Diffusion with reaction in the receiving phase in which a reagent is usually added in order to make the solute concentration effectively zero at the membrane internal phase interface, thus maximizing the concentration gradients across the membrane. It is used for removal and/or recovery of compound such as phenol, acetic acid, ammonia and amines. It is also called Type I Facilitation mechanism.
c) Type II Facilitation mechanism. Mass transfer assisted by a certain carrier present in the membrane phase as well as ion concentration gradient between the two sides of the membrane phase. This mechanism is used for the recovery and enrichment of heavy metal ions as illustrated in Figure 2.6.

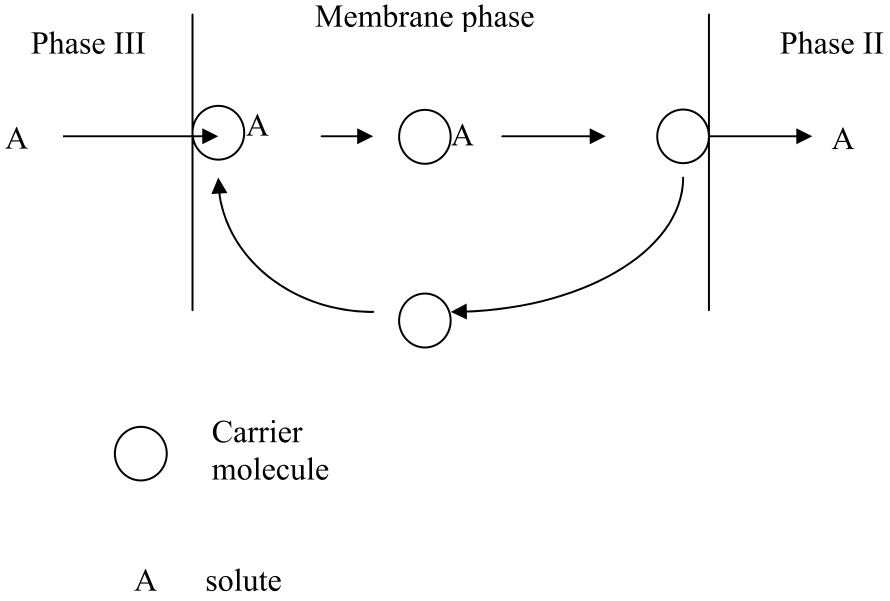


Figure 2.6: The mechanism of couple transport in liquid membrane.

From the above transfer mechanisms, Type II facilitation mechanism will be considered in this study because of its suitability for metal separation. The carrier species may be incorporated into the organic solvent in the membrane phase and this gives rise to carrier-mediated transport. In this mechanism, the carrier molecule can selectively and reversibly react with the solute. The reversible reaction provides a means of enhancing the solute flux and improving the selectivity at the same time.

In type II facilitation, also called carrier-facilitated transport, the diffusing species are carried across the membrane phase by a carrier compound or extractant. Reaction of the diffusing species and the carrier compound takes place both at the external interface, between external and membrane phases, and the internal interface, between the membrane and internal phases.

The following are the separation steps in couple transport of ‘carrier facilitated’ mechanism:

- Mass transfer of metal ion from external bulk phase through mass transfer resistance film to external interface between external phase and membrane phase.
- Metal ion (M^{2+}) reacts with the carrier or extractant (HR) of the membrane phase at the interface of external and membrane phase.

$$M^{2+}\big|_{\text{external}} + 2HR \rightarrow MR_2\big|_{\text{interface (external/membrane)}} + 2H^{+}\big|_{\text{external}}$$

- Mass transfer of MR_2 in the membrane phase from the external/membrane interface to the membrane/internal interface

$$MR_2\big|_{\text{interface (external/membrane)}} \qquad MR_2\big|_{\text{interface (membrane/internal)}}$$

- Membrane-soluble complex (MR_2) at the membrane/internal interface reacts with hydrogen ions from the internal phase.

$$MR_2\big|_{\text{interface (membrane/internal)}} + 2H^{+}\big|_{\text{internal}} \rightarrow 2HR\big|_{\text{interface (membrane/internal)}} + M^{2+}\big|_{\text{internal}}$$

The metal ions are released from the membrane phase into the internal phase.

- Mass transfer of extractant in the membrane phase from the membrane/internal interface to the external/membrane interface that mean the free carrier diffuses back.

$$HR\big|_{\text{interface (membrane/internal)}} \qquad HR\big|_{\text{interface (external/membrane)}}$$

The facilitated transfer of metal ions occurs when pH value of the internal phase is lower than that of the external phase. That means the concentration difference of protons between the two aqueous phases provides the driving force for the separation and produces the counter-transport of metal ions. Through this mechanism, the mass transfer driving force can be maintained even if the concentration of the solute in the receiving phase is higher than in the feed solution/phase.

2.2.6 Liquid Membrane Application

Since the invention of liquid surfactant membranes by Li in 1968, metal ion extraction using liquid membranes has received considerable interest. The process is capable of achieving a higher concentration of metals in fewer stages while maintaining the high selectivity of solvent extraction.

For the last two decades this method has attracted many studies in the area of hydrometallurgy such as separation of metal ions either from waste or from ores (Reis and Carvalho, 1993; Reed *et al.*, 1987; Marr, 1984; Draxler and Marr, 1986; Babcock *et al.*, 1986). It has been reported recently that emulsion liquid membrane system has been successfully used to recover copper selectively from waste stream of mine solutions (Wright *et al.*, 1995).

Separation of metals using emulsion liquid membrane was studied by many researchers in previous publications (Nakashio, 1993). From the viewpoint of practical application in hydrometallurgy and waste-water treating processes, recovery processes for copper (Volkel *et al.*, 1980; Goto *et al.*, 1989a), uranium (Hayworth *et al.*, 1983) and zinc (Marr, 1984) were examined in test plant. The first application of emulsion liquid membrane (ELM) on an industrial scale was the process to remove zinc from waste water at a textile plant in Austria (Draxler and Marr, 1986).

On the other hand, over the years a number of investigators concentrated on separation of gases using liquid membrane especially supported liquid membrane. The mechanism is carrier mediated facilitated transport. Some of the areas in which this technique has been applied include production of oxygen-enriched air (Johnson *et al.*, 1987), CO removal by tert-amine macrocyclic (Koval *et al.*, 1985), CO_2

removal from gas mixture (Saha and Chakma, 1992) and removal of SO_2 using water as carrier (Teramoto *et al*., 1999).

Liquid membrane can also be used as chemical reactors for the reaction between two gases in a heterogeneous catalyst system where the reactants are encapsulated in an aqueous membrane containing catalyst. As the gasses diffuse through the membrane, the reaction occurs and the products diffuse out into the external receiving solvent. One application of the process is the catalytic oxidation of ethylene to acetaldehyde. Others include oxidation of propylene to acetone, oxidation of acetaldehyde to acetic acid and carbonylation of methanol with CO to acetic acid.

In biotechnology, liquid membrane system has been used in many applications of biochemical and biomedical process. In biochemical study this technology has been used for the extraction of amino acid (Scheper *et al*., 1987; Itoh *et al*., 1990). Scheper *et al*. (1987) used a quaternary ammonium carrier in emulsion liquid membrane for enzyme catalyzed preparation of L-amino acids. Kuo and Gregor (1983) and Kiani *et al*. (1984) used immobilized liquid membranes to extract acetic acid from aqueous solution while Friesen *et al*. (1991) used liquid membrane for extraction of citric acid.

In biomedical process liquid membrane was used in blood oxygenation and artificial red blood cells; for extracorporeal oxygenation of blood, bubbles of gaseous O_2, encapsulated in a fluorocarbon liquid membrane are made to contact oxygen-depleted blood. During the contact, oxygen diffuses from the membrane into the blood while CO_2 diffuses in the opposite direction and is swept out (Frankenfeld *et al*., 1978). In preparation of artificial blood cells, liquid membrane serves as template for the formation of the artificial cells. A liquid membrane system can also be used to remove phenolic toxins from blood during liver failure where internal trapping consist of an aqueous solution of the enzymes (Volker *et al*., 1982).

2.2.7 Demulsification

Demulsification is one of the key processes for emulsion liquid membrane application. Demulsification is mainly used for removing water and salts from crude oil in oil industry, and for the recovering the membrane phase including organic solvent, surfactant, extractant, and valuable solute ions in waste treatment processes. The common methods of demulsification are centrifugation, sedimentation, thermal breaking, and the electrostatic method.

Thermal breaking requires a lot of energy to break emulsion droplets and cannot be applied to all emulsions because of the thermal instability of some components. Centrifugation involves high mechanical work input and high investment costs. Systems with very small droplets and little density difference between the dispersed and the continuous phases are unable to be separated by conventional breaking methods (Strathman, 2001). In contrast to conventional methods, electrical emulsion breaking works at room temperature, involves no moving parts, maintain low energy input and enables the separation of small droplets from the continuous phase (Byers and Amarnath, 1995; Luo *et al.*, 2001; Strathman, 2001).

The electrostatic method in a high voltage field is one of the most effective and simplest demulsification methods. Electrostatic forces cause the coalescence of dispersed water droplets and their growth into larger drops, which then fall readily due to electric forces or gravity. In DC field, the electrophoretic droplet motion enhances the probability of coalescence, whereas greater motion in the bulk fluids is necessary to increase coalescence in an AC field (Byers and Amarnath, 1995; Ibrahim *et al.*, 2001; Kim *et al.*, 2002; Luo *et al.*, 2001). According to Taylor (1988), the major effects of exposing dispersed water drops to high-strength AC fields include drop deformation and drop-drop attraction, resulting from polarization of the drops. These effects are different when DC fields are applied, establishing electrophoretic motions, which can lead to an increase in drop-drop collision rate. Furthermore, Bailes and Larkai (1981) suggested that the varying rates of drops collision caused by the breaking and formation of drop chains are frequency dependent.

The parameters of the electro demulsification process are voltage, frequency, temperature, degree of mixing, emulsion shape, and distance of electrodes, density and viscosity of emulsion, interfacial tension, water drop size, size distribution, hold up, surfactant concentration in the oil phase, and electrolyte concentration in the continuous phase (Ibrahim *et al*., 2001; Ivanov and Kralchevsky, 1997; Kim *et al*., 2002; Lu *et al*., 1997; Strathman, 2001; Wang *et al*., 1994). The electrostatic demulsification process is based on the coalescence and precipitation of water droplets. Although the electrostatic method has a relatively wide application, the mechanism of electrical coalescence is not well understood because of the complexity of hydrodynamic and electrical phenomena of interfacial polarization (Benavente and Jonsson, 2000; Luo *et al*., 2001; Strathman, 2001). The electric field acts only at the interface between droplets and the continuous phase rather than throughout the bulk of the phases (Benavente and Jonsson, 2000). The diameter of the internal droplets of emulsion has a great influence on both the critical electric field intensity and the demulsification rate (Lu *et al*., 1997).

From the above review, generally the coalescence of droplets consists of three steps:

i) The flocculation step, in which the dispersed droplets of the internal phase flocculate into some large group, but the drops still exist without coalescence due to the electrostatic force;
ii) The coalescence step, in which the drops in the group coalesce into a larger drop, resulting in the decrease in the number of drops;
iii) The sink step, in which the large internal drops sink by gravity to the interface between oil and water, and coagulate into the water phase, resulting in the breakdown of emulsion.

The electrical effect primarily affects the first step. This illustrates the increasing rate of motion of the droplets in an electric field (Harpur *et al*., 1997; Ivanov and Kralchevsky, 1997; Lu *et al*., 1997).

2.3 Emulsion Liquid Membrane Extraction of Silver

2.3.1 Carrier Selection

Extractant is the main factor in determining the efficiency of any extraction process. Therefore, it is very important to develop an efficient mobile carrier for a target metal ion, and the choice of the carrier often decides the success of the process. As a suitable carrier of emulsion liquid membrane, the following conditions are required;

i) High selectivity for metal to be separated
ii) React reversibly with the metal so that the metal can be recovered by a stripping reaction
iii) high extraction rate at the external interface of the emulsion globules
iv) high stripping rate at the interface of the internal water droplets in the emulsion.
v) Have a very low solubility in the aqueous phases for economic and environmental reason.

Based on conventional solvent extraction and liquid membrane processes, several type of extractant were used in metal extraction as reported in literature and summarized in Table 2.4.

Table 2.4: Extractant Used in Metals Extraction Using Conventional Solvent Extraction (CSE), Emulsion Liquid Membrane (ELM) and Supported Liquid Membrane (SLM) Processes.

Type of Extractant	Metal Ions	Feed Solution	Method	Surfactant	Stripping Solution	Diluent	References
GROUP 1							
Cyanex 272	Cu	$CuSO_4$	ELM	ECA 5025 DNP-8	6 N H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
	Ni	$NiNO_3$	ELM	ECA 5025 DNP-8	6 N H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
	Zn	$ZnSO_4$	ELM	ECA 5025 DNP-8	6 N H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
			SLM[a]		4.5 M HNO_3	Kerosene	Kanungo and Mohapatra (1995)
			SLM[a]		HCl	Dodecane	Cox and Bhatnagar(1990)
	Ag	$AgNO_3$	CSE		H_2SO_4	Xylene/Hexane	Sole *et al.* (1994)
	U	Pure	SLM[a]			n-Dodecane	Chiarizia (1991)
Cyanex 302	Ag	$AgNO_3$	CSE			Kerosene	Alam *et al.* (1997)
		$AgNO_3$	CSE		HCl	Xylene/Hexane	Sole *et al.* (1994)
	Cd	Pure Cd	SLM[b]			Kerosene	Alonso *et al.* (1997)
Cyanex 301	Ag	$AgNO_3$	CSE			Kerosene	Alam *et al.* (1997)
		$AgNO_3$	CSE		HCl	Xylene,Hexane	Sole *et al.* (1994)
D2EHPA	Ni	$NiCl_2$	ELM			Kerosene	Shiau and Jung (1993)
		$NiSO_4$	SLM[a]		HNO_3	Kerosene	Juang (1993)
			SLM[a]		5-6 M HNO_3	n-Dodecane	Zha and Fell (1995)
	Te	$TeCl_4$	ELM	Span 80	1.6-2.2 M	Kerosene	Chakraborty&Datta (1994)
	Sr	$SrCl_2$	ELM	Span 80	HNO_3 HNO_3	Kerosene	Inci *et al.* (1993)
			SLM[a]		HNO_3	Kerosene	Chaudry *et al.* (1994)
	Ag	$AgNO_3$	ELM	Span 80	HCl	Toluene	Izatt *et al.* (1988)
		$AgNO_3$	ELM	Span 80	HNO_3	Kerosene	Lee *et al.* (1996)
	Pb	$Pb(NO_3)_2$	ELM	Span 80	H_2SO_4	Toluene	Izatt *et al.* (1988)
	An		ELM	Span 80	HCl	Kerosene	Shen *et al.* (1996)
	Zn	$ZnCl_2$	ELM		H_2SO_4	Kerosene	Shiau (1991)
		$ZnSO_4$	ELM	ECA5025 DNP-8	H_2SO_4	Tetradecane	Bhavani (1994)
	Cu	$CuSO_4$	ELM	ECA5025 DNP-8	HCl	Tetradecane	Bhavani *et al.* (1994)
	Co	$CoSO_4$	SLM[a]		H_2SO_4	Kerosene	Juang (1993)
	Cd	$CdCl_2$	ELM		HNO_3	Kerosene	Shiau and Jung (1993)
DEHPA	Zn	$ZnSO_4$	ELM	Span80, ECA 4360	HNO_3	n-Dodecane	Bart *et al.* (1995)
	Cd	Pure	ELM	Span 80		Paraffin oil	Gabriel & Abraham(1999)
		Rare earth	SLM[a]	Flat sheet	H_2SO_4	n-Dodecane	Kopunec & Manh (1993)
PC-88A	Co	$CoSO_4$	ELM	PX 100 Span 80	H_2SO_4	n-Heptane	Kasaini *et al.* (1998)
	Ni	$NiSO_4$	ELM	PX 100 Span 80	H_2SO_4	n-Heptane	Kasaini *et al.* (1998)
	Zn	$ZnCl_2$	ELM	Span 80	water	n-Heptane	Goto *et al.* (1991)
		Rare earth	SLM[a]		HNO_3	Kerosene	Kojima *et al.* (1994)
		Rare earth	SLM[b]		H_2SO_4	n-Heptane	Kubota *et al.* (1995)
DEHMTPA	Zn	$ZnSO_4$	ELM	Span 80 ECA 4360	Thiourea	n-Dodecane	Bart *et al.* (1995)
MSP-8	Pd	Simulated waste	ELM	Span 80,		n-Heptane	Kakoi *et al.* (1996)
	Ag	Ag nitrate	CSE		H_2SO_4	Kerosene	Alam *et al.* (1997)
LIX 65N	Cu	Cu salt	ELM	ECA4360	H_2SO_4	n-Heptane	Goto *et al.* (1989a-b)
		Cu salt	ELM	Span 80		Kerosene	Volkel *et al.* (1980)

Table 2.4: Continued

Type of Extractant	Metal Ions	Feed Solution	Method	Surfactant	Stripping Solution	Diluent	References
LIX 984	Cu	$CuSO_4$	ELM	ECA 5025 DNP-8	H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
			SLMa		H_2SO_4	Kerosene	Yang & Fane (1997)
	Ni	$Ni(NO_3)_2$	ELM	ECA5025 DNP-8	H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
	Zn	$ZnSO_4$	ELM	ECA5025 DNP-8	H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
LIX 860	Cu	$CuSO_4$	ELM	ECA5025 DNP-8	H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
	Ni	Ni $(NO_3)_2$	ELM	ECA5025, DNP-8	H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
	Zn	$ZnSO_4$	ELM	ECA5025 DNP-8	H_2SO_4	Tetradecane	Bhavani *et al.* (1994)
LIX 64N	Cu	Cu salt	ELM	Span 80	H_2SO_4	Kerosene	Volkel *et al.* (1980)
	Zn	$ZnCl_2$	ELM		HCl	Kerosene	Shiau & Jung (1993)
	Cd	$CdCl_2$	ELM		HCl	Kerosene	Shiau & Jung (1993)
	Ni	$NiCl_2$	ELM		HCl	Kerosene	Shiau & Jung (1993)
LIX 63	Cu	Cu salt	ELM	Span 80	0.25-2.5MH_2SO_4	Kerosene	Volkel *et al.* (1980)
Acorga P17	Cu	Cu salt	ELM	Span 80	2.3 M H_2SO_4	Kerosene	Volkel *et al.* (1980)
Acorga P50	Cu	Cu salt	ELM	Span 80	2.3 M H_2SO_4	Kerosene	Volkel *et al.* (1980)
			SLM		1-2 M H_2SO_4	n-Octane	Szpakowska (1996)
AcorgaM5640	Cu	Cu $(NO_3)_2$	CSE		2 M H_2SO_4	Kerosene	Alguacil *et al.* (2002)
KELEX 100	Cu	Cu salt	SLM		0.5-2 M H_2SO_4	n-Octane	Szpakowska & Nagy (1997)
		Cu salt	ELM	Span 80	2.3 M H_2SO_4	Kerosene	Volkel *et al.* (1980)
			ELM	Span 80	2.3 M H_2SO_4	Kerosene	Volkel *et al.* (1980)
SME 529	Cu	Cu salt	SLM^a		H_2SO_4	Kerosene	Zha *et al.* (1995)
LIX 84	Cu	Cu salt	SLM^b		H_2SO_4		Yi &Taviarides (1995)
GROUP 2							
PrimeneJMT	Ag	Ag salt	ELM^b		H_2SO_4	Tetradecane	Hu &Wiencek (1998)
	Cr	$CrSO_4$	CSE			Kerosene	Sanuki *et a*l. (1999)
Tridecyl-amine	Au	Gold cynide	CSE			Xylene	Caravaca *et al.* (1996)
Amberlite	Cr	$CrSO_4$	SLM^a		NaOH	n-Dodecane	Chiarizia (1991)
	Co	$CoSO_4$	SLM^a		NaOH	n-Dodecane	Chiarizia (1991)
	Ni	Ni salt	SLMa			Kerosene	Marchese *et al.* (1995)
Alamine336	Cu	Cu salt	SLMa		Distilled water	Kerosene	Marchese *et al.* (1995)
	Cd	Cd salt	SLMa		Distilled water	Kerosene	Marchese *et al.* (1995)
	Cr	Cr(III)&(VI)	SLM^a		Distilled water	o-Xylene, Kerosene	Molinari *et al.* (1989)
TOA	Hg	$HgCl_2$	ELM	Span 80	NaOH	Toluene	Li *et al.* (1996)
	Cr	Cr salt	SLM^b		NaOH	Xylene	Guha *et al.* (1994)
	Fe	Fe salt	SLM^b		NaOH	Xylene	Yun *et al.* (1993)
	Co	$CoSO_4$	SLM^a		NH_4OH	n-Dodecane	Kalachev *et al.* (1992)
Adogen 364	Pt	Pure	SLM^a		NH_4OH	n-Dodecane	Kalachev *et al.* (1992)
	Cd	Pure Cd	SLM^a			Kerosene	Fu *et al.* (1995)
			ELM	Span 80	NaOH	Dimethyl-Benzene	Li *et al.* (1998)
Aliquat 336	In		SLM^a		AcONa	Kerosene	Rosell *et al.* (1997)
	Mo	Na-Mo salt	ELM	Monesan	NaOH	Kerosene, Heptane, Xylene, Dodecane	Prashant & Kumar (2002)
	Cr	Cr ion	SLM^a		NaOH	Kerosene	Mahmoud *et al.*(1996)
		Cr ion	ELM	Span 80	NaOH	Kerosene	Bhowal & Datta (2001)
		Cr(IV)	SLM^a		LiCl	Kerosene	Molinari *et al.* (1989)
		Cr(IV)	SLM^b		NaCl	Kerosene	Ortiz *et al.* (1996)

Table 2.4: Continued

Type of extractant	Metal ions	feed Solution	Method	Emulsifier	Stripping Solution	Diluent	References
Aliquat 336	Cr		SLM				Alonso *et al*. (1996)
	U	Granite ore	ELM	Span 80	Na_2CO_3 /$(NH_4)_2CO_3$	Kerosene	Maysa (2003)
GROUP 3							
MIBK	Ag	AgNO3	CSE				Chormann (1985)
TBP	Rare		SLM^a		HCl	n-Dodecane	Kopunec & Manh (1992)
	earth		SLM^a		HNO_3	Kerosene	Chitra *et al*. (1997)
	U		SLM^a		NH_4CO_3	Kerosene	Chaudry *et al*. (1995)
			SLM^a		HCl	Dodecane	Shukla & Misra (1991)
TOPO	Pt		ELM		HCl	Toluene	Sharad & Purushottam (2001)
	Rare		SLM^a			Kerosene	Chitra *et al*. (1997)
	earth		SLM^a			n-Dodecane	Manh & Kopunec (1992)
Cyanex 923	Cr	Cr(IV)	SLM^a		NaCl/HCl	Xylene	Alguacil *et al*. (2000)
	Au	Aucyanide	SLM			Xylene	Alguacil *et al*. (2002)
	Ti	$Cu_2(SO_4)_3$	CSE		0.4 M HCl	Xylene	Saji *et al*. (1998)
	Pt	K_2PtCl_6	CSE		HCl	Toluene	Sharad & Purushottam (2001)
Cyanex 921	Au	Aucyanide	SLM			Xylene	Alguacil *et al*. (2002)
Cyanex 471X	Ag	$Ag(NO_3)_2$	CSE			Toluene,Xylene Benzene, Hexane	Hubicki & Hubicka (1995)
	Pt	K_2PtCl_6	CSE		HCl	Toluene	Sharad & Purushottam (2001)
Crown ether							
H18C6	Ag	$AgNO_3$	SLM		$Na_2S_2O_3$	Chloroform	Mojtaba (2000)
	Ag	$AgNO_3$	CSE			Chloroform	Lachowicz *et al*. (2002)
D16C4	Ag	$AgNO_3$	CSE			Chloroform	Ouchi *et al*. (1999)
Bis(benzothia crownether)	Ag	$AgNO_3$	CSE		H_2SO_4	Chloroform	Kimura (1987)
Cyclic-tetrathioether	Ag	$AgNO_3$	CSE		Acid		Saito *et al*. (1998)
Calixarence							
Calix[4]arene	Pb	$Pb(NO_3)_2$	CSE		Acid	Chloroform	Ohto *et al*. (1999)
	Ag	Silver salt	CSE				Kumar *et al*. (2003)
		Silver salt	CSE			CH_2Cl_2	Jean *et al*. (2001)
	Rare earth	Lanthanide Chloride	ELM	$2C_{18}\Delta^9GE$	H_2SO_4	Toluene	Kakoi *et al*. (1997)
Ketonic	Ag	$AgNO_3$	CSE		H_2SO_4	Chloroform	Ohto *et al*. (1997a)
	Pd	$Pb(NO_3)_2$	CSE		H_2SO_4	Chloroform	Ohto *et al*. (1997a)
Carboxyl	Rare earth	Lanthanide Chloride	ELM	$2C_{18}\Delta^9GE$	H_2SO_4	Toluene	Kakoi *et al*. (1997)
p-tert-butyl calixarenes	Na	NaOH	ELM		DI water	CH_2Cl_2+CCl_4	Ye *et al*. (1999)
	K	KOH	ELM		DI water	CH_2Cl_2+CCl_4	Ye *et al*. (1999)
p-tert-octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	$2C_{18}\Delta^9GE$	H_2SO_4	Toluene	Kakoi *et al*. (1997)

Note:

Group 1	Ion Compound Formation Extractant
Group 2	Ion Association Extractant
Group 3	Solvating Extractant

2.3.2 Parameters Affecting on ELM Extraction Process

The parameters that affect the extraction rate of the emulsion liquid membrane are; membrane thickness (Kim *et al*., 1997); temperature and concentration of external and internal phase (Teramoto *et al*., 1983); volume ratio of external phase to emulsion liquid membrane (Lin and Long, 1997); volume fraction of internal phase, surfactant and the carrier (Kakoi *et al*., 1997; Lee *et al*., 1997; Mok and Lee, 1994); and the speed of the agitator (Lin and Long, 1997; Teramoto *et al*., 1983).

The other parameter is membrane stability. The stability of the emulsion is one of the critical issues for extraction processes using emulsion liquid membrane. If the emulsion liquid membrane is unstable, the emulsion globules are broken, which will reduce the efficiency of the membrane extraction. The major factors affecting the emulsion liquid membrane stability are agitation speed, viscosity, temperature and pH of external phase, volume and concentration of internal phase and composition of membrane phase (Bechers, 1985; Daneisi *et al*., 1981; Szpakowska & Nagy, 1991).

The addition of the surfactant increases the stability of the ELMs and the membrane thickness, but it decreases the rate of the diffusion process. With an increase in temperature, the extraction rate also increases. The speed of agitation affects the extraction rate to a great extent. Initially, the extraction rate increases due to the increase in the mass transfer coefficient in the aqueous phase; but with time, the extraction rate decreases due to the hydrodynamic instability of membrane at a higher agitator speed, leading to the breakage of the membrane.

In liquid membrane technology, the surfactant is the most important component in the emulsion liquid membrane process. It determines not only the stability of the emulsion but also influences a lot of other parameters like osmosis and water solubility and often represents a high mass transfer resistance (Draxler and Marr, 1986). Commercial surfactants which are commonly used are complex compounds that have hydrophilic and lipophilic groups, the latter orienting the molecules towards the organic membrane phase. The ratio of the two groups, called the hydrophilic-lipophilic balance (HLB) determines the kind of emulsion obtained. If HLB is less than about 10, 'water-oil-water' emulsions are obtained; surfactants with larger HLB values favor 'oil-water-oil' emulsion (Patnaik, 1995). Two commercial surfactants are SPAN 80 and ECA 4360 or a mixture thereof.

There are many papers concerning the effect of surfactant on the behavior of the emulsion (Goto *et al.*, 1989b; Dreher *et al.*, 1999). Membrane breakage in emulsion liquid membrane system includes the rapture of the emulsion and the leakage of the internal reagent and extracted solute through the membrane phase to the external phase. As a result, the membrane breakage causes a decrease of driving force for mass transfer and an increase of the raffinate concentration, thereby lowering the extraction efficiency (Wan and Zhang, 2002). Therefore the type of surfactant used in emulsion liquid membrane process has very strong effect on extraction rate (Goto *et al.* 1991). It has been noted that surfactant influences the emulsion stability and the transport rate of the solute. By increasing the surfactant concentration, the emulsion stability will improve; however the extraction rate will decrease due to the presence of more surfactant molecules at the reaction site (aqueous-organic interface).

2.3.3 Thermodynamics of Extraction

Thermodynamics is a branch of science dealing with energetic of substances and process (Rydberg *et al.*, 1992). Thermodynamics determines the driving potential for a system to change from one state to another such as whether a chemical reaction will proceed and how far it will proceed (Clifford *et al.*, 1976). The general extraction reaction of a metal ion (M^{n+}) with extractant (HR) was explained by:

$$M^{n+} + \overline{nHR} \leftrightarrow \overline{MR_n} + nH^{+} \qquad (2.2)$$

2.3.3.1 Distribution Ratio

The amount of metal extracted is determined by analysis of the aqueous (raffinate) after extraction process. The distribution ratio of a metal between an aqueous phase and organic phase is known as the distribution coefficient, D and is defined as:

$$D = \frac{\text{concentration of extracted metal into organic phase}}{\text{concentration of unextracted metal in the aqueous phase}} \qquad (2.3)$$

Equation 2.2 can be written as the rate, or velocity at which $[M^{n+}]$ and $\left[\overline{nHR}\right]$ react and this reaction is proportional to their concentration:

$$v_f = k_f\left[M^{n+}\right]\left[\overline{nHR}\right] \qquad (2.4)$$

where, v_f is the velocity of the forward reaction which produces the reaction products $\left[\overline{MR_n}\right]$ and $\left[H^+\right]^n$, and k_f is the proportionality constant.

The rate of reverse reaction can be written as following:

$$v_r = k_r\left[\overline{MR_n}\right]\left[H^+\right]^n \qquad (2.5)$$

where at equilibrium, $v_f = v_r$

$$v_f = k_f\left[M^{n+}\right]\left[\overline{nHR}\right] = v_r = k_r\left[\overline{MR_n}\right]\left[H^+\right]^n \qquad (2.6)$$

From Equation 2.6, the equilibrium constant (K_E) is defined as:

$$K_E = \frac{\left[\overline{MR_n}\right]}{\left[M^{n+}\right]} \cdot \frac{\left[H^+\right]^n}{\left[HR\right]^n} = \frac{k_f}{k_r} \qquad (2.7)$$

So, equilibrium constant, K_E can be written as;

$$K_E = D\left(\frac{[H^+]}{[\overline{HR}]}\right)^n \tag{2.8}$$

$$D = K_E\left(\frac{[\overline{HR}]}{[H^+]}\right)^n \tag{2.9}$$

From Equations 2.7, 2.8 and 2.9 it is clear that the extraction of metal in these systems is mostly dependent on the concentration of the extractant in the organic phase and on the pH of the aqueous phase, and is independent on the total metal ion concentration.

Taking logarithms of Equation 2.9, the following equation will obtain:

$$\log D = \log K_E + n\log[\overline{HR}] - n\log[H^+] \tag{2.10}$$

Equation 2.10 can also write as:

$$\log D = \log K_E + n(\log[\overline{HR}] + pH) \tag{2.11}$$

The plots of log D versus (log $[\overline{HR}]$ + pH) will give a straight line of slope n and the intercept is equal to log K_E. An expression involving pH can be explained by the following equations:

$$\frac{1}{n}\log D = \frac{1}{n}\log K_E + \log[\overline{HR}] + pH \tag{2.12}$$

or

$$pH = \frac{1}{n}\log D - \frac{1}{n}\log K_E - \log[\overline{HR}] \tag{2.13}$$

If the aqueous / organic ratio is 1, this means if 50% of metal is extracted into the organic phase, therefore D = 1 and log D = 0, Equation 2.13 will give;

$$pH = -\frac{1}{n}\log K_E - \log\left[\overline{HR}\right] \tag{2.14}$$

The pH given in Equation 2.14 is known as $pH_{0.5}$ or pH_{50}. The increase in extractant concentration will result in decrease in $pH_{0.5}$.

2.3.3.2 Recovery Efficiency, E

The recovery efficiency is defined as:

$$E(t) = 1 - \frac{C_e(t)}{C_{eo}} \tag{2.15}$$

where;

$C_e(t)$ = Concentration of solute in the external phase (mol/l)

C_{eo} = Initial concentration of solute in the external phase (mol/l)

By rearranging Equation 2.15 and equating in terms of the equilibrium constant of Equation 2.9, the following equation will get;

$$D = \frac{E}{1-E} = K_E \frac{\left[\overline{HR}\right]^n}{\left[\overline{H^+}\right]^n} \tag{2.16}$$

2.3.3.3 Separation factor

Separation factor ($S_{Mi/M2}$) of any system containing metal (1) and metal (2) can be defined as:

$$S_{M1/M2} = D_1 / D_2 \tag{2.17}$$

where, D_1 and D_2 represent two extraction coefficients of metals (1) and (2) respectively. This indicates the degree to which the two metals can be separated. Generally the higher the separation factor, the higher the performance of metal separation. In multi component system, separation factor of metal (1) to other metal can defined as:

$$S_{M1/Mi} = D_1 \Big/ \sum_{i=2}^{n} D_i \tag{2.18}$$

2.3.4 Modeling of Emulsion Liquid Membrane Extraction

2.3.4.1 Modeling of Equilibrium Conditions

Mathematical modeling of extraction processes using liquid membranes are based on either membrane approach or integral approach. For the first it is assumed that the total resistance of the transfer process is on the liquid membrane phase. In this case the processes occurring in the other two phases are not considered. In the integral approach the extraction system is assumed to be an integrated closed system of three interacting liquids. The concentration gradients and volume changes in the three phases are thus taken into account.

Whatever the approach used, the equilibrium conditions at the two interfaces are usually described by the distribution coefficient of the solute between the organic and aqueous phase as discussed in Section 2.3.3.1, which is assumed to be constant if the extraction/stripping process is operated in a continuous mode, leading to small changes in the concentration during the process (Coelhoso *et al.*, 1997). However, if the system is operated in a batch mode of operation, there will be a large variation of solute concentration in each phase leading, in some cases, to a high variation of the distribution coefficient.

This dependency of the distribution coefficient on the solute concentration must be considered as it affects the driving force for mass transfer and consequently the corresponding mass transfer coefficient. If there is a variation of the distribution coefficient with solute concentration, then the solute flux and mass transfer coefficients must be included in the kinetic model in order to correctly evaluate the mass transfer coefficients. The distribution coefficient, D, can only be considered constant if $K_e = 1$ or if the change of the aqueous solute concentration during the extraction (or the stripping) process is in the linear region of the equilibrium curve. The deviation between the values of the mass transfer coefficients calculated by using either a variable distribution coefficient or a constant distribution coefficient depends on the region of the equilibrium curve considered. The higher deviations on the mass transfer coefficients take place when the equilibrium curve diverges from linearity.

On the other hand, reactive metal extraction depends on both the kinetics of chemical reactions taking place in the system and the rates of mass transfer of the species between the two liquid phases. If the extraction rate is diffusion-controlled, it will depend on the interfacial area and the concentration of the slow-diffusion species. When the extraction rate is chemically controlled, it is necessary to ascertain the location of the rate-controlling chemical reaction.

2.3.4.2 Emulsion Liquid Membrane Extraction Models

Most investigations on liquid membrane mass transfer concentrate on the facilitated transport within the emulsion globule (i.e. permeation with chemical reaction or carrier transport with reaction). Hence several mathematical models have been proposed on the basis of these grounds to predict mass-transfer rate and separation efficiency. Usually, the emulsion liquid membrane separation systems have been analyzed on the basis of the different configurations of the emulsion globule, depending on the degree of sophisticated in handling the permeation mechanism.

Based on the disposition of the interfacial resistances to mass transfer in the system, these models can be classified into two different groups.

i) Models without Radial Profile of Concentration

It is assumed that all the fine droplets within the emulsion are coalesced into a single large droplet, and this droplet is encapsulated in a membrane film. Mass transfer of the solute takes place by diffusion across a flat membrane of constant thickness into an internal interface, where it reacts with the reagent. Mass transfer is proportional to the average concentration difference between the external continuous and the internal phases. According to the membrane geometry, two different models have been developed in the literature: Uniform flat-sheet model (Kremesec, 1981; Kremesec and Slattery, 1982) and hollow-sphere model (Matulevicius and Li, 1975; Hochhauser and Cussler, 1975).

ii) Models with Radial Profile of Concentration

A microscopic view of the liquid membrane system shows two key features that must be adequately described in a realistic model of transport and the reaction in the system. The first is the emulsion heterogeneity resulting from the presence of the droplets of internal reagent dispersed in the emulsion globules, while the second is the non-uniform size distribution of the globules themselves.

The solute diffuses through the external phase to the aqueous/membrane interface, where it reacts with the carrier. The formed complex diffuses through the oil membrane of the emulsion globule into the encapsulated aqueous phase that is immobilized due to the presence of surfactant, the internal circulation being negligible within the globules where the complexes react instantaneously with the internal reagent. Two different approaches have been reported.

a) The immobilized globule model (Teramoto *et al.*, 1981, 1983; Bunge and Noble, 1984). This model represents the composite nature of the emulsion globule and removes the restriction of irreversibility of the stripping reaction. The reaction reversibility precludes the reaction-advancing front since there is no separate reacted and unreacted region. Solute diffusing into the emulsion globule reacts with the internal reagent or distributes itself between the two phases. The product formed inside the encapsulated droplets may give the reverse reaction, producing unreacted solute that can diffuse back into the membrane. Thus it is possible that solute diffuses to the center of the globule without contacting the internal reagent or through a series of forward and reverse reaction steps.

b) Advancing front model (Ho *et al.*, 1982; Kim *et al.*, 1983). In this model the stripping reaction is assumed to be instantaneous and irreversible. Hence the solute is unable to penetrate into the globule beyond those droplets, which are completely depleted of reagent. It is then immediately removed by reaction with the internal reagent. Thus, there must exist a sharp boundary, or reaction front at which the reaction takes place, which separates the region containing no solute from the outer region that contains no reagent. As the reagent is consumed by the reaction, this reaction front advanced into the globule. It is assumed that the reaction products are immobilized and hence that they are incapable of back-diffusion.

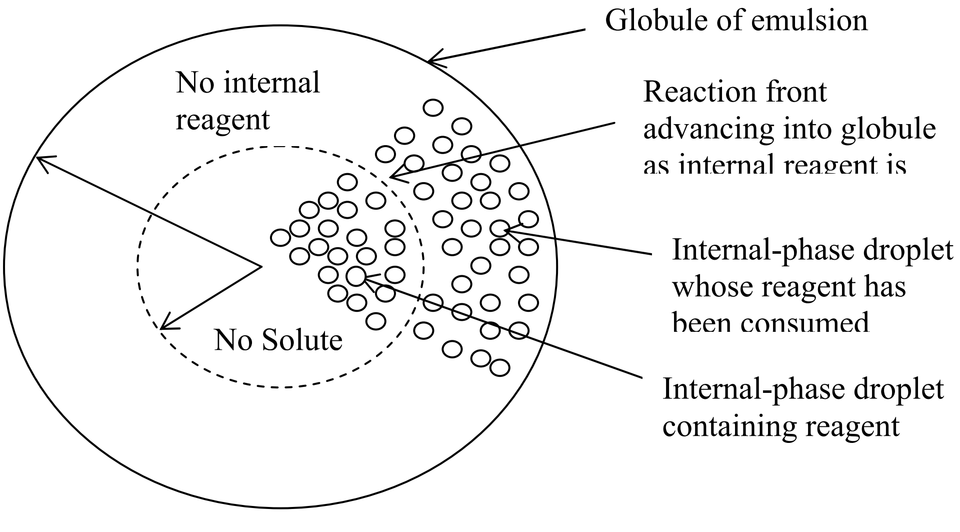


Figure 2.7: Schematic diagram of the advancing front model (Ho *et al.*, 1982).

The velocity of the advancing front is determined by the permeation resistances in the emulsion drop. In order to react at the advancing front, solute has to be transported;

- across the outer boundary layer
- across the surfactant monolayer at the outer phase boundary
- across the layer of pure membrane phase and, finally either
- through pure membrane and/or
- through receptor phase plus membrane phase (on this path, additional resistances of surfactant must be considered.

In the transport model, the three outer resistances are lumped together into one global resistance giving one overall mass transfer coefficient. All resistance of the heterogeneous regions are also lumped together into one global resistance giving one effective diffusivity, D_{eff}.

2.3.4.3 Models of Type II ELM Extraction

A great deal of research has been done to model emulsion liquid membrane extraction since it was developed by Li in 1968 as a unique method for the separation and concentration of such solutes as metal ions, weak bases, weak acids and amino acids. The most promising application among them is the concentration of metal ions by the carrier-mediated transport. The first authors to propose this Type II film model were Hochhauser and Cussler (1975) followed by Lee *et al.* (1978), Kondo *et al.* (1979), Volker *et al.* (1980) and Frankenfeld *et al.* (1981). These researchers work on copper removal and developed a planar film model.

Another model presented for Type II emulsion liquid membrane separation is by Hayworth *et al.* (1983). Considering steady state condition with no breakage, this model agreed with the data of the removal of uranium from phosphoric acid streams. Meanwhile, Lorbach and Marr (1987) attempted the modeling of mass transfer of zinc with bis(2-ethylhexyl)-dithiophosphoric acid . A mass transfer model for carrier-facilitated transport is developed which is based on the extraction and stripping reaction as well as on the transient diffusion of the loaded carrier molecules into an emulsion globules.

However, very few studies have been reported in the literatures on carrier-facilitated transport specifically on the leakage or membrane breakage (Teramoto *et al.*, 1983). In fact, the breakage of the membrane is still considered as one of the most serious obstacles in the successful application of liquid membrane to industrial application. Following a few researches concerning emulsion breakage, Lee *et al.* (1996) develop a general physical model of typical batch system for the extraction of silver and called it the permeation model. The model takes into account the extraction reaction between the silver ion and the carrier molecules at the external interface, the diffusion of the complex in the membrane phase, the stripping reaction at the internal interface and the reaction of silver ion with the reagent in internal phase. It also considered the leakage of the internal aqueous phase to the external aqueous phase due to membrane breakage.

2.3.5 Engineering Aspect of Process Equipment

There is no special equipment for the batch extraction (mixer-settler) except the equipment for the formation of the emulsion as shown in Figure 2.2. The emulsion is mixed with the bulk phase in a small scale container. The extraction efficiency will be measured by change in the amount of solute remaining in the bulk phase with time. The emulsion is formed by mixing the organic phase and the internal phase with the high speed agitation. Most researchers used high speed homogenizer in making emulsion.

In continuous extraction, stirred column is widely used in the industrial application. A counter current stirred column is shown in Figure 2.8, where the stirrer includes three blades due to the height of the column. The emulsion enters the column from the bottom of the column, and the continuous bulk phase flows from the top to the bottom. The emulsion is dispersed in the continuous bulk phase by agitation. Because of the effect of buoyancy, the emulsion will float on the top of the column and leave the column. Extraction of the solutes takes place when emulsion continuously contacts the continuous bulk phase. Furthermore, in contrast, the continuous bulk phase will silk to the bottom of the column and leave the column.

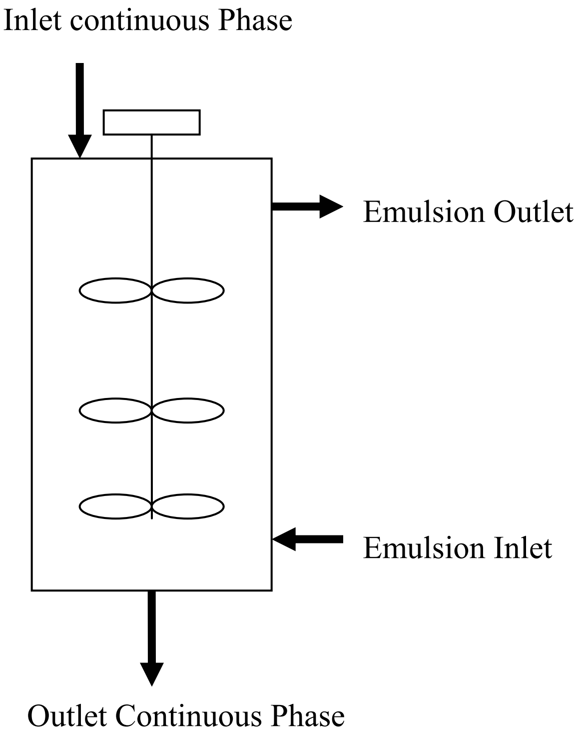


Figure 2.8: The counter-current stirred column (Lin, 1996).

Another type of extraction column type is spray column as shown in Figure 2.9. This equipment was investigated by Kataoka *et al*. (1987). In this column, one or many nozzles are equipped on the bottom of the column. The flow direction of the emulsion and the continuous bulk phase is similar to that in the stirred column. The only difference between them is that the dispersion of the emulsion in the continuous bulk phase is done by spraying from the nozzle.

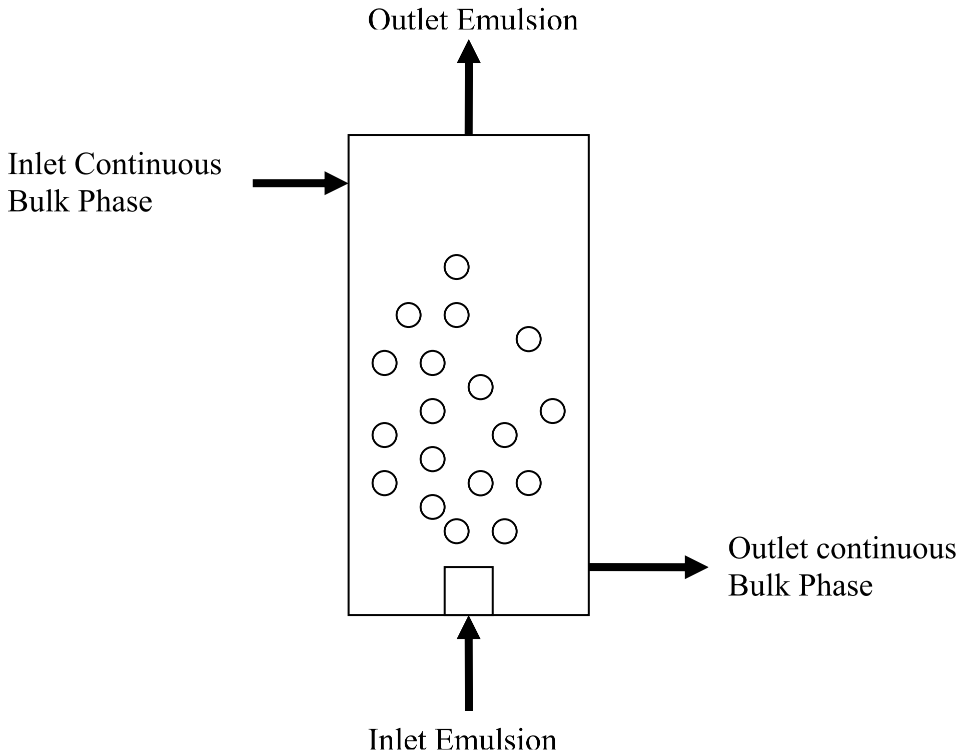


Figure 2.9: The counter-current spray column (Kataoka *et al.*, 1987).

The industrial process using the stirred column is shown in Figure 2.10. The industrial emulsion liquid membrane system includes four important basic units: emulsification, extraction, settling, and demulsification. The demulsifier is used to break the emulsion and the organic phase is recycled to the emulsification unit.

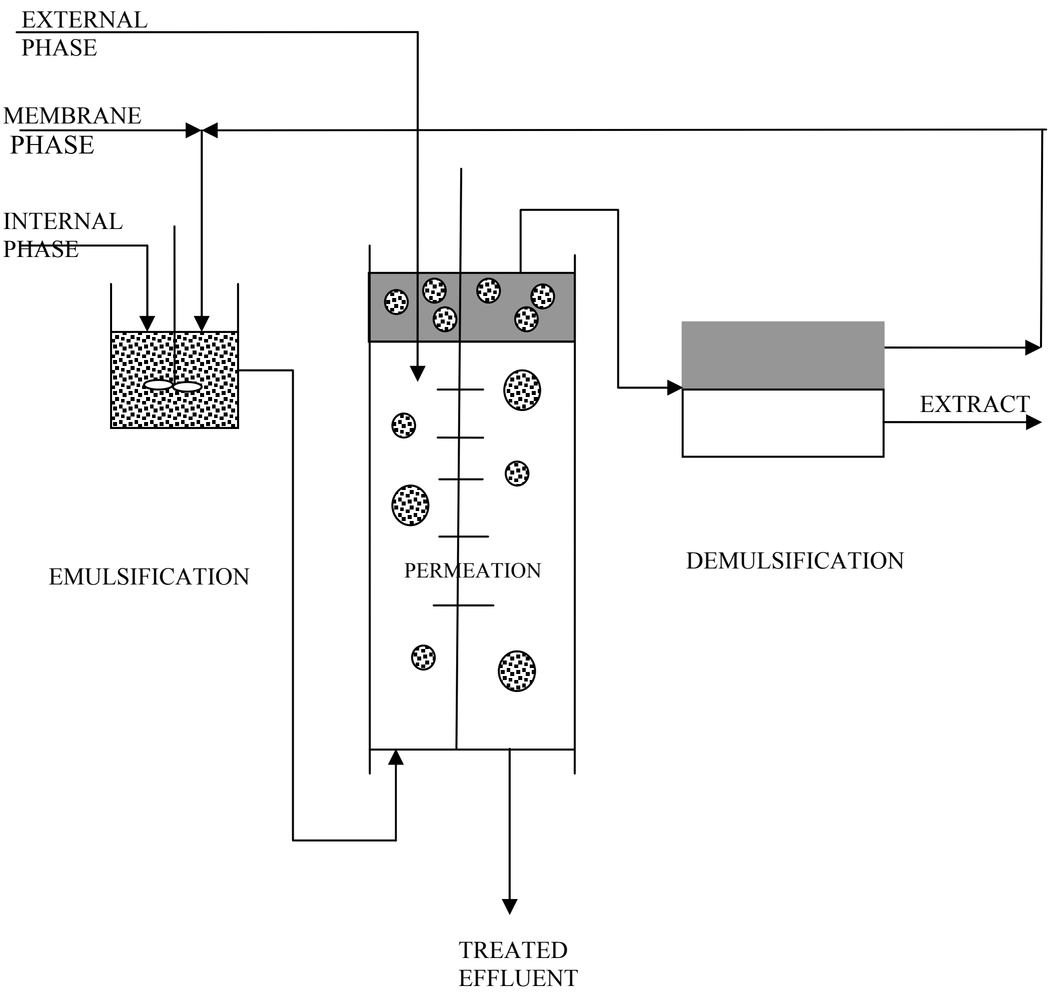


Figure 2.10: Industrial process using stirred column (Lin, 1996).

CHAPTER 3

MATERIALS AND METHODS

3.1 Solvents and Reagents

3.1.1 Chemical Used in Carriers Screening

The extractants used were ordered from various suppliers as shown in Table 3.1. All the extractants were dissolved either in kerosene, toluene or chloroform as diluents and were obtained from Fluka Chemika, Merck (M) Sdn. Bhd. and Surcchem Products LTD respectively. All extractant and diluents are manufacture grade and used as received.

3.1.2 Chemical Used in Stripping Agents Screening

Hydrochloric, nitric, and sulfuric acids, thiourea and sodium thiosulphate were used as stripping agents. All chemical used are analytical grade and used as received.

Table 3.1: List of extractants used for silver extraction from photographic waste.

Extractant	Chemical Formula	Product
Triisobutylphosphine sulfide (Cyanex 471X)	$C_{12}H_{27}PS$	Fluka
Diisooctylthiophosphinic acid (Cyanex 302)	$C_{16}H_{35}OPS$	Fluka
Diphenylthiocarbazone (Dithizone)	$C_{13}H_{12}N_4S$	Acros
Trioctylamine (TOA)	$C_{24}H_{51}N$	Fluka
Bis(2-ethylhexyl) phosphate (D2EHPA)	$C_{16}H_{35}O_4P$	Fluka
Tri-n-octylphosphine oxide (TOPO)	$C_{24}H_{51}OP$	Sigma
Tributylphosphate (TBP)	$C_{12}H_{27}O_4P$	Fluka
Diisooctylphosphinic acid (Cyanex 272)	$C_{16}H_{35}O_2P$	Fluka
8-Hydroxychinolin	C_9H_7NO	Merck
Tridodecylamine (Adogen 363)	$C_{36}H_{75}N$	Acros
Methyltrioctylammonium chloride (TOMAC)	$C_{25}H_{54}\ ClN$	Fluka
Tetramethylthiuram disulfide	$C_6H_{12}N_2S_4$	Acros

Table 3.2: List of stripping agent used in screening process.

Stripping agent	Purity (%)	Company
Hydrochloric acid	37	Merck
Nitric acid	70	Merck
Sulfuric acid	95 – 97	Merck
Thiourea	98.5	Riedel-de Haën

3.1.3 Membrane Components

Cyanex 302 and tetramethylthiuram disulfide (Thiuram) were obtained from Sigma and ACROS Organic respectively. Some of the properties of these extractants are tabulated in Table 3.3.

Table 3.3: Properties of Cyanex 302 and Thiuram.

Extractant Property	Cyanex 302	Thiuram
Physical appearance	Light yellow Mobile liquid	White powder
Molecular weight (g/mol)	306.49	240.41
Assay (%)	85	97
Density (g/cm^3)	0.93	1.30
Temp. (decomp.) (°C)	337	156

Span 80 (obtained from Fluka Chemica) was used as a surfactant or emulsifying agent in this research. Kerosene and toluene obtained from Fluka Chemika and Merck (M) Sdn. Bhd. were used as diluents. Thiourea in acidic solution used as stripping agent was obtained from Riedel-de Haen. All extractants, surfactant and diluents are manufacture grade and used as received.

3.1.4 Photographic Waste Samples and Characterizations

The photographic waste samples used in this research were taken from photographic shop at Taman Universiti, Skudai, Johor. This waste is the mixture of fixing and bleaching stages in photo processing. The photographic waste sample is very sensitive to temperature and light. Therefore, it was kept in the refrigerator to prevent any ageing effect or sedimentation of the sample constituents.

The metal contents in the photographic wastes were measured using the Atomic Absorption Spectrophotometer (AAS). The anion contents in the photographic waste samples were measured using Ion Chromatography model LC 20 with electric chemical detector model ED40. The pH measurements were carried out using pH meter model Cyberscan 100. The determination of the kinematics viscosity, v was carried out by using Programmable Rheometer Brookfield Model DV-III at room temperature. The density (ρ) of the photographic waste samples was measured using hydrometer.

3.2 Experimental Procedures

3.2.1 Liquid Membrane Component Selection

Liquid membranes consist of four main components such as carrier, stripping agent, diluents, and surfactant. Several types of carrier and stripping agent as reported in literature were chosen to screen out the potential components in extracting silver in emulsion liquid membrane process.

3.2.1.1 Carrier Screening

Carrier screening experiments are intended to choose the appropriate carrier to recover silver. The main parameter of interest is the amount of silver extracted. Therefore the suitable carrier must have high tendency to form complexes with silver ion and also easy to strip out with stripping agent. The affecting parameters such as the effect of carrier concentrations and initial pH were studied in this research.

The extraction process was carried out by mixing an equal volume (20ml) of aqueous photographic wastes and organic solutions using a mechanical shaker with rotation at 250 rpm for a period of one day (24 hours). Then, the mixture is carefully poured into separation funnel. After the phase separations (around 15-30 minutes), an aqueous phase was carefully separated from the organic phase. The pH equilibrium is measured. The procedures are repeated for different carrier types. The concentration of silver in the aqueous phase after extraction is measured by using AAS. The concentration of silver extracted in the organic phase is calculated based on mass balance principle. All experiments were carried out at room temperature (26 ^{o}C).

3.2.1.2 Stripping Agent Screening

This experiment is designed to identify the types and optimum strip agent concentration required to strip silver from silver loaded organic solution. Stripping process is the reverse extraction step. Therefore, organic phase (silver loaded organic phase) is taken from extraction process from Section 3.2.1.1. An equal volume of strip agent at specified concentration and silver loaded organic phase were mixed by using mechanical shaker for 18 hours at 250 rpm and then carefully poured into a separation funnel and left for phase separation for about 15-30 minutes. After phase separation is completed, the aqueous phase was carefully separated to avoid any contamination by the organic phase and concentration of silver stripped were measure by AAS. The stripping procedures are repeated for other strip agents and concentrations.

3.2.1.3 Stability Test

The intension of this experiment is to choose an appropriate emulsifier concentration to stabilize the emulsion during the experiments. Stability test were conducted on surfactant, Span 80, where each compound differs in the amount in organic phase. Equal volume of organic and stripping phases was mixed by using high speed homogenizer (13500 rpm) for 5 minutes. After that, this white emulsion was transfer to graduated test tubes to measure the volumes of free oil, emulsion and water for a few days. These tests were conducted at room temperature, 26°C. The same procedures were repeated for different speed of homogenizer, type of diluents in organic phase and type of carriers.

3.2.2 Emulsion Liquid Membrane Extraction

3.2.2.1 Emulsion Liquid Membrane Preparation

The formulation of emulsion liquid membrane consists of four important components such as diluent, carrier, emulsifier/surfactant, and stripping solution. The organic phase (diluent, carrier, and emulsifier) is prepared by dissolving required concentration of carriers and surfactant with appropriate diluents. The selective carrier of silver from Section 3.2.1.1 was dissolved in diluent at 0.05 M concentration and 5 % (w/v) of Span 80 as surfactant was added to the solution to form an organic phase or membrane phase.

The emulsion was prepared by emulsifying aqueous solutions (stripping phase) of certain acidity (from Section 3.2.2.1) with formulated organic phase. An equal volume of 5 ml portions of organic and aqueous solutions was stirred continuously at 13500 rpm using motor driven homogenizer for 5 minutes to obtain a stable white emulsion liquid membrane. After that, the emulsion is cold down to room temperature and is ready for the extraction study. The average mean diameter of emulsion is measured using a microscope with camera. The emulsion must be freshly prepared each time before the extraction experiment.

3.2.2.2 Extraction Study

The external phase, shown in dark brown colour in Figure 3.1, was prepared by using real photographic waste without any pre-treatment. The prepared emulsion is then dispersed into the agitated vessel with the external solution in a volume ratio of emulsion to feed phase of 1 to 5. The three-phase dispersion was stirred for 20 minutes. After that, the samples were quickly introduced into a separation funnel and left for phase separation. The aqueous phase was filtered in order to remove any entrainment and this phase was analyzed by using AAS.

The loaded emulsion phase was demulsified in electrostatic coalescer by applying a certain value of voltage. After all the emulsion broke down, the solution were left for phase separation in separation funnel. The metal concentrations in aqueous phase are measured using AAS and the organic phase is ready for the recycle process. The same procedures were repeated for different agitation speeds, and different liquid membrane formulation including type of diluents, carriers and emulsifier concentration.

For emulsion breakage study, the three phase mixture was run separately at different time of extraction such as 1, 3, 5, 7.5, 10, 15 and 20 minutes. The procedures are the same as the extraction study. After extraction, the samples are quickly introduced into the separation funnel to separate the emulsion from the aqueous feed phase. After phase separation, an emulsion phase was introduced into graduated test tubes to measure the volume of emulsion phase. The emulsion breakage was calculated by the difference of emulsion volume at initial and after extraction.

3.2.2.3 Demulsification Study

After the liquid membrane extraction, the internal droplet phase should be taken out for recovering the solutes. The demulsification step using physical treatments was applied. This demulsifying method was conducted by using an electric field across the electrode to break up the emulsion. The applied electric field strength is increased gradually from low to high since all the emulsion was demulsified.

A model of batch demulsifier was equipped with a glass-insulated electrode. Water heater was used as outer jackets to control the temperature of the system. Saturated NaCl solution was put in the outer glass as the outer electrode. The inner glass cylinder was filled with emulsion and glass coated stainless steel rod was placed in the center of the glass cylinder to serve as the inner electrode. The wall thickness of the glass cylinder was 1 mm. The diameter of stainless steel rod was 10 mm. For continuous system the demulsifier was fabricated based on tubular coalescer model (Goto *et al.*, 1989) with a few modifications to allow greater electric field especially for high voltage power supply equipments.

Demulsification experiments were performed by applying a pulsed AC field with electric potential 40 kV (30- 800 Hz) across the outer and inner electrode. The specification of high voltage demulsifier is shown in Table 3.4. The time for phase separation was measured by a stop watch.

Table 3.4: Specification of High Voltage Demulsifier.

Power Supply

Input : 240 V
Output : 0-22 V
Current : 6 Amp
Frequency : 60 Hz

High Voltage Power Supply

Input : 0-22 V
Output : 0-40 kV
Frequency : 30 – 800 Hz

Accessories

Oscilloscope
High voltage probe

3.3 Analytical Procedures

3.3.1 Metal Content Analysis

Analysis of the metal content is performed to characterize the photographic wastes as well as to determine the metal concentration in the aqueous phase after extraction and stripping process and also ELM recovery process. The metals were determined by using Atomic Absorption Spectrophotometer (AAS) model Philips PU9200X. AAS is principal tool for measuring metallic elements at ppm level. A liquid sample is sucked through a plastic tube into a flame, and then the flame evaporates all liquid, breaks all molecules into atoms, and excites many atoms into high energy states. The concentration of elements was measured by absorption of light from atoms in flame. In most cases, for silver analysis the samples were diluted to the concentration of between 2 – 8 ppm in order to bring it to within the linear working range of the equipment sensitivity. All data presented in this thesis were an average of triplicates results.

3.3.2 Anion Content Analysis

The anion contents in the photographic waste samples were measured using Ion Chromatographic model LC 20 with electric chemical detector model ED40. Since the anion concentration in the waste is high, the samples were diluted using distilled water. This procedure is very important to avoid any blocking in the column. This ion Chromatography is very sensitive especially for most common inorganic strong acid anions such as chloride, nitrate, phosphate, and sulphate. All measurements were carried out in triplicates and all data presented are average values.

3.3.3 pH Measurement

PH of every samples and photographic waste were measured using pH meter (Ecomet P25 Bench pH/mV/TEMP meter, Istek, INC). The pH meter was calibrated with a three point calibration using purchased buffer solutions. All measurements were carried out at room temperature.

3.3.4 Viscosity Measurement

The viscosity of the membrane phases was determined for experiments where it was necessary to estimate the diffusivities of various membrane components. Viscosity determinations were made on a Programmable Rheometer Brookfield Model DV-III at room temperature. Viscosity was measured by taking the rate of change of shear stress versus strain. A spindle type 18 was used to test the viscosity and motor speed at 100 rpm.

3.3.5 Density Measurement

Density (ρ) measurements were made of aqueous solutions, pure membrane components, blended membrane phase, diluents for particle size measurements and emulsions. All the density measurements were conducted at 30 ± 1°C using hydrometer.

3.3.6 Emulsion Drop Size Measurement

The drop size of emulsion was measured using a microscope with camera and directly connected to Video Structure Image Analyzer. One drop of emulsion was placed on glass slide and by using microscope with camera a few photo were captured. The photo was analyzed and an average diameter of emulsion droplets was calculated.

CHAPTER 4

LIQUID MEMBRANE COMPONENT SELECTION

4.1 Introduction

In finding a good formulation of liquid membrane, detail observation in choosing a potential carrier of silver and stripping agent must be carried out in a batch emulsion liquid membrane process. As we know, silver in photographic waste is widely available for recovery. However the selective extraction of silver(I) from thiosulfate solutions has not been exhaustively investigated due to the tight bonding between silver and thiosulfate ions. So far, work performed on evaluating solvent extraction techniques for thiosulfate solution is limited to amine extractants (Strestrom, 1992) and tetramethylthiuram disulfide (Mendoza and Kamata, 1996). In order to find a good carrier of silver from thiosulfate medium, several types of extractant were screened based on the conventional solvent extraction process.

Solvent extraction is a process that involves the transfer of a solute from one liquid phase to another liquid phase. The two liquid phases must be immiscible to each other. In the context of metal recovery from photographic wastes, the metal-bearing aqueous feed solution is brought into contact with the solvent containing certain extractant for a sufficient period of time. The metal of interest which is initially insoluble in the organic phase is transferred from the aqueous phase into the organic phase through the formation of an uncharged species that is soluble in the organic phase with certain mechanism (Chapman, 1987).

The metal loaded organic phase is then mixed with an aqueous phase to undergo the stripping process. The stripping process is actually the reverse reaction of extraction. The metal of interest is stripped from the organic phase by suitable aqueous solution. The extractant in the organic phase can thus be recovered and reused for the extraction process (Freiser, 1973).

The effectiveness of an extraction process is influenced by some typical factors, such as types of carrier/extractant and its concentration, pH and selectivity of extractant. As for stripping process, the types of stripping agent used and their concentrations are of paramount concern. Hence, these parameters are studied in this research to examine their effects on silver extraction from photographic wastes. On the other hand, the main process condition in emulsion liquid membranes must be considered thoroughly in term of emulsion stability and extraction capacity.

4.2 Carrier Screening

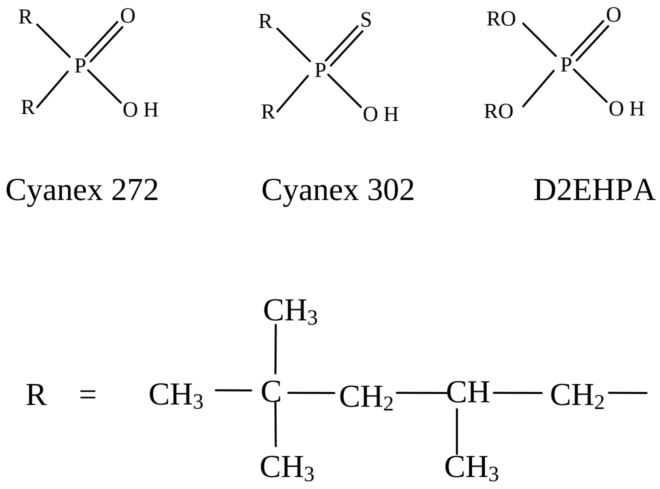
The factors that need to be considered in metal selectivity and capacity of extraction are the selection of carrier types and its concentration. High selectivity and capacity can only be achieved by selecting the right carrier and its concentration for target metal ions. An increase in carrier concentration will increase the extraction capacity, but to what extent needs to be optimized to avoid excessive use of carrier that is normally very costly.

From the above point of view a few experiments have been carried out to select the suitable carrier in liquid membrane formulation. The carriers to be assessed consist of acidic, chelating, basic and solvating extractants.

4.2.1 Acidic Extractants

Three types of acidic extractants such as Cyanex 272, Cyanex 302, and D2EHPA were examined in term of their capability and selectivity in extracting metals from photographic wastes. The chemical structures of these extractants are shown in Figure 4.1. Table 4.1 and Table 4.2 show the extraction performance of metals using 0.005 M and 0.05 M extractant concentration. The result indicates that extractant containing P=S functional groups (Cyanex 302) provide a higher extraction towards silver than other metals that existed in the photographic waste compared to Cyanex 272 and D2EHPA. The extractions of silver with Cyanex 302 are 18% and 97% when using 0.005 M and 0.05 M respectively. This finding is inline with reports by Alam *et al*. (1997), who investigated the extraction of silver with some commercial sulfur-containing extractant like MSP-8, Cyanex 301, Cyanex 302 and SFI-6R. On the other hand, Cyanex 272 and D2EHPA also exhibit good metal extraction but it is only selective to iron for Cyanex 272 and no significant selectivity for D2EHPA.

The result also shows that there is no significant difference in pH equilibrium of each extractant even though the amount of metal-complexes formation depends on the types of extractant. As reported in literatures, acidic extractants are monobasic in nature and thus release one hydrogen ion for every molecule which combines with a metal while the number of molecules of extractant involved in the formation depends on the oxidation state or coordination number of the metal ions (Tait, 1993; Sole and Hiskey, 1995; Sole *et al*., 1994; Alam *et al*., 1997; Almela and Elizalde, 1995). However silver extraction from photographic wastes occurred at a relatively higher equilibrium pH. This may be caused by the buffering effect of metals and organic compounds present in the photographic waste.



Cyanex 272 Cyanex 302 D2EHPA

R represents the 2,4,4-trimethylpenyl groups

Figure 4.1: Chemical structure of acidic extractant (Ritcey and Ashbrook, 1984).

The general reaction for the extraction of metal cation, M^{n+} with D2EHPA, Cyanex 272 or Cyanex 302 can be written as following equation, where these extractants form dimer in an organic diluent (Sole and Hiskey, 1995; Ritcey and Ashbrook, 1984; Kim *et al.*, 1995):

$$M^{n+} + \frac{m}{2}\overline{(HR)}_2 \leftrightarrow \overline{MR_n(m-n)HR} + nH^+ \qquad (4.1)$$

where, M^{n+} is the metal ion in the aqueous phase, $\overline{HR}$ is the extractant, $\overline{MR_n(m-n)HR}$ is the metal complex, and nH^+ is the amount of hydrogen ion which is released during forming the metal complex.

Table 4.3 shows the separation factor of silver over the other metals in photographic wastes. The result presented showed that Cyanex 302 conferring the highest value of separation factor than Cyanex 272 and D2EHPA over the other metals; indicates that Cyanex 302 is very selective to silver. Therefore, a larger extraction distribution coefficient, D means a better extraction performance.

Table 4.1: Metal extraction of photographic wastes without pH adjustment (Experimental conditions: [Carrier] = 0.005 M, agitation speed = 250 rpm, and T = 26 ºC).

Group	Extractant	Diluent	pH_{eq}	% Extraction (0.005 M)			
				Ag	Na	K	Fe
Acidic	Cyanex 272	Kerosene	8.32	1.46	0.00	0.30	22.60
	Cyanex 302	Kerosene	8.04	18.10	0.00	0.00	0.00
	D2EHPA	Kerosene	8.64	0.00	2.65	8.16	15.63
Chelating	8-hydroxy Chinolin	Kerosene	8.50	0.00	2.49	4.34	11.41
	Diphenyl Thiocarbazone (Dithizone)	Chloroform	8.02	20.37	0.00	1.31	0.00
	Tetramethylthiuram disulfide	Chloroform	8.20	72.83	14.06	23.43	5.94
Basic	Adogen 363	Chloroform	8.55	0.74	0.00	8.57	0.00
	TOMAC	Kerosene	8.40	3.53	14.77	10.50	21.64
	Trioctylamine (TOA)	Kerosene	8.26	41.99	0.00	94.63	0.00
Solvating	Cyanex 471X	Kerosene	8.29	21.62	22.79	23.23	29.96
	Tri-n-octylphosphine oxide (TOPO)	Kerosene	8.30	0.90	3.47	4.73	16.30
	Tributylphosphate (TBP)	Kerosene	8.22	8.08	0.00	2.79	0.00

Table 4.2: Metal extraction of photographic wastes without pH adjustment (Experimental conditions: [Carrier] = 0.05 M, agitation speed = 250 rpm, and T = 26ºC).

Group	Extractant	Diluent	pH_{eq}	% Extraction (0.05 M)			
				Ag	Na	K	Fe
Acidic	Cyanex 272	Kerosene	8.34	14.04	0.00	20.77	42.20
	Cyanex 302	Kerosene	8.34	97.18	0.65	5.68	5.74
	D2EHPA	Kerosene	8.29	0.00	46.26	46.98	53.49
Chelating	8-hydroxy Chinolin	Kerosene	8.15	0.00	0.00	0.00	67.37
	Dithizone	Chloroform	8.21	90.92	0.00	0.00	0.00
	Tetramethylthiuram disulfide	Chloroform	8.15	99.88	17.06	6.50	20.19
Basic	Adogen 363	Chloroform	8.31	0.00	0.00	1.16	0.00
	TOMAC	Kerosene	8.28	23.93	4.98	4.06	1.79
	Trioctylamine (TOA)	Kerosene	8.30	8.47	8.42	0.00	19.96
Solvating	Cyanex 471X	Kerosene	8.33	2.96	0.03	0.20	0.00
	Tri-n-octylphosphine oxide	Kerosene	8.30	18.81	3.96	2.82	0.00
	Tributylphosphate (TBP)	Kerosene	8.13	23.73	5.09	7.86	3.64

Table 4.3: Extraction selectivity of silver from photographic wastes using acidic extractants (Initial concentrations: [Ag] = 2490.52 ppm, [Fe] = 1478.91 ppm, [K] = 6238.06 ppm, [Na] = 3628.63 ppm).

Extractant	$S_{Ag/Fe}$	$S_{Ag/K}$	$S_{Ag/Na}$	$S_{Ag/(Fe,K,Na)}$
Cyanax 272	0.22	0.62	0.00	0.16
D2EHPA	0.22	0.62	0.00	0.00
Cyanex 302	567.00	573.00	5250.00	270.00

4.2.2 Chelating Extractants

There are three different types of chelating extractant; 8-hydroxy Chinolin, dithizone and tetramethylthiuram disulfide which were investigated to study their capability in extracting silver from photographic wastes. Dithizone was the first chelating reagent used for metal ion extraction, and it is still one of the most important chelating extractants. The chemical structure of dithizone is shown in Figure 4.2. Its capability in extracting silver from photographic wastes is proved to be 90% with 0.05 M dithizone concentration and very selective to silver. However, the difficulty of using dithizone in this extraction process is the colour of organic solution which is dark and almost similar with the colour of a real photographic waste solution. Thus during the experimental observation, it must be difficult to distinguish the liquid membrane phase and the feed aqueous solution. Furthermore, dithizone is insoluble in kerosene which is less toxicity and water solubility solvent.

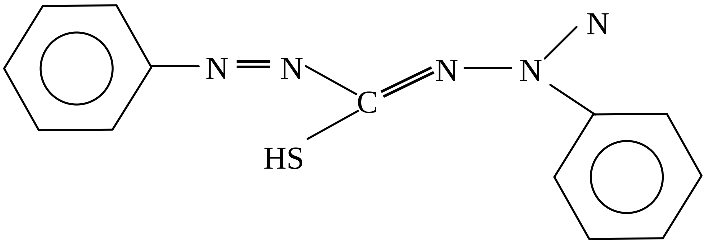


Figure 4.2: The chemical structure of diphenylthiocarbazone (Dithizone).

8-hydroxychinoline has also been studied as a silver extractant. The result shows that 8-hydroxychinoline is very selective to iron. It can extract iron around 67% with 0.05 M extractant. However they can exist in ionic form both in acid and basic aqueous solutions. Thus, these reagents in an organic solvent are readily transferred into the aqueous phase at any pH. It is also noted that these reagents perform, in many cases as self-adduct chelates (Stary, 1963). Furthermore, the dark green colour of the third phase was also observed between the aqueous and organic phases. This is due to high solubility of diluents into the aqueous phase.

One of promising chelating extractants is tetramethylthiuram disulfide. The extraction of silver was very high even at a low concentration of tetramethylthiuram disulfide. The result shows that 73% of silver was extracted with 0.005 M concentration. With 0.05 M the extraction of silver was almost 100%. It is expected that this is due to the existence of excess ‘free extractant’ in the process. In addition, tetramethylthiuram disulfide is also very selective to silver. However, this reagent only dissolved in a polar solvent like chloroform, toluene or dichloroethane. Therefore, safety and environmental regulations make it less preferable in extractant selection especially in global era.

The general reaction for the extraction of metal cation, M^{n+} with chelating extractant can be written as following equation;

$$M^{n+} + n\overline{HA} \leftrightarrow \overline{MA_n} + nH^+ \tag{4.2}$$

where, M^{n+} is the metal ion in the aqueous phase, $\overline{HA}$ is the extractant, $\overline{MA_n}$ is the metal complex, and nH^+ is the amount of hydrogen ion which is released during the formation of the metal complex.

Table 4.4 shows the separation factor of silver over the other metals in photographic wastes. The result presented showed that tetramethylthiuram disulfide and dithizone conferring the highest value of separation factor than 8-hydroxy chinolin over the other metals.

Table 4.4: Extraction selectivity of silver from photographic wastes using chelating extractants (Initial concentrations: [Ag] = 1750 ppm, [Fe] = 1250 ppm, [K] = 5320 ppm, [Na] = 3980 ppm).

Extractant	$S_{Ag/Fe}$	$S_{Ag/K}$	$S_{Ag/Na}$	$S_{Ag/(Fe,K,Na)}$
8-hydroxy Chinolin	0.00	0.00	0.00	0.00
Dithizone	∞	∞	∞	∞
Tetramethylthiuram disulfide	3290	12000	4050	1580

4.2.3 Basic Extractants

Metal extraction by a basic extractant or also called neutral extractant has grown into one of the most promising tools in aqueous separation chemistry and is still increasing. Three types of basic extractants such as Adogen 363, TOMAC, and TOA were chosen to test their capability in extracting metal ions from photographic waste solution. Table 4.1 and 4.2 show that the extractions are very poor for all types of extractant at 0.005 M and 0.05 M concentration. Although the extractive power toward metals increases from primary to higher degree of amines (Ritcey and Ashbrook, 1984), the results show no significant effect of these amines even for TOMAC as quaternary amines. It is due to many factors affecting the chemistry of metal extraction by amines such as the influence of the diluents employed, the aqueous media and types of ionic compounds, and the structure of the amine itself.

Extraction of metal, M^{2+} which forms an anionic complex with an anion A^- in the aqueous phase, by an amine salt, $R_3N.HA$ can be presented as an anion exchange process (Ritcey and Ashbrook, 1984);

$$MA_m^{(m-n)-} + \overline{(m-n)(R_3N.HA)} \leftrightarrow \overline{(R_3N^+H)_{m-n}MA_m^-)} + (m-n)A^- \qquad (4.3)$$

In order to achieve this exchange the amine must first be converted to an appropriate salt to provide an anion to exchange with the metal species, but this is not absolutely necessary for an anionic metal species. Table 4.5 shows the separation factor of silver from photographic waste using different types of basic extractant. The results show that the separation factor of extractants are very low; meaning that no capable extractant was found from this group of extractants

Table 4.5: Extraction selectivity of silver from photographic wastes using basic extractants (Initial concentrations: [Ag] = 2384 ppm, [Fe] = 1490 ppm, [K] = 3710 ppm, [Na] = 4991 ppm).

Extractant	$S_{Ag/Fe}$	$S_{Ag/K}$	$S_{Ag/Na}$	$S_{Ag/(Fe,K,Na)}$
Adogen 363	0.00	0.00	0.00	0.00
TOMAC	17.30	7.40	6.00	2.80
Trioctylamine (TOA)	0.25	∞	1.00	0.37

4.2.4 Solvating Extractants

There are three types of solvating extractants go through the screening process in finding a capable extractant in extracting silver from the photographic waste solution. Table 4.1 shows that no extractant provides any significant selectivity to any metals. TBP only extract 8% of silver with 0.005 M concentration and 26% with 0.05 M but it also competes with iron. In this process the originality of photographic wastes was maintained and no pH effect was studied. Sekine and Hasegawa (1977) reported that extraction of silver from a nitric acid solution using TBP is poor. However, extraction of silver in hydrochloric acid is good at low acid concentration.

Another potential extractant attempted by Rydberg *et al.* (1992) is Cyanex 471X. It can extract silver ion from chloride, nitrate, or sulfate media selectively from copper, lead and zinc. Hubicki and Hubicka (1995) also found that Cyanex

471X could extract silver from a nitrate solution. However, in this study extraction of silver from photographic wastes using Cyanex 471X was very poor even at 0.05 M concentration and shows no capability in metal ion selection. This trend of result is almost similar to that of TOPO. No significant performance stability was recorded when using low and high concentration of extractant. It is due to the tight bonding of silver complexes in photographic wastes rather than the interaction of extractant-silver complexes and the effect of original pH solution in the system. As reported by Mihaylov and Distin (1992) the chemical behavior of TBP and TOPO is similar regarding the dependency on acidity whereas at low acidity, the principal extracted species depends on the extent of loading. However, a metal-TOPO complex forms at high acidity (Kondo *et al*., 1997). Unfortunately, this research only attempted the extractant capability on the real photographic waste with is around pH 8. Table 4.6 shows the separation factor of silver from photographic waste using different types of solvating extractant. The results show that the separation factor of silver over other metals is low, indicate that no selectivity and capacity of silver were obtained using these extractants.

Table 4.6: Extraction selectivity of silver from photographic wastes using solvating extractants (Initial concentrations: [Ag] = 3520 ppm, [Fe] = 1080 ppm, [K] = 4480 ppm, [Na] = 251 ppm).

Extractant	$S_{Ag/Fe}$	$S_{Ag/K}$	$S_{Ag/Na}$	$S_{Ag/(Fe,K,Na)}$
Cyanex 471X	∞	14.82	9.99	5.97
Tri-n-octylphosphine oxide (TOPO)	∞	7.97	5.62	3.30
Tributylphosphate (TBP)	8.23	3.65	5.80	1.76

4.3 Carrier Selection

According to the results presented in Section 4.2, Cyanex 302 was chosen for detail studies on silver extraction from photographic wastes. It is due to the potential of this acidic extractant to extract silver. In addition to the good performance, Cyanex 302 is readily dissolved in kerosene, which has very low toxicity. The other promising extractants are chelating extractants such as dithizone and tetramethylthiuram disulfide providing a good potential of silver extraction but it doesn’t dissolve in kerosene. Meanwhile, the problem with dithizone is the colour of liquid dithizone which is quite similar to the colour of liquid photographic wastes. This will cause problem in phase separation. Therefore, the following section will discuss further the effect of pH and extractant concentration of Cyanex 302 and tetramethylthiuram disulfide as a promising extractant in the emulsion liquid membrane process.

4.3.1 Cyanex 302

All acidic extractants used in solvent extraction processes liberate hydrogen ions during the extraction process (Ritcey and Ashbrook, 1984). The greater the amount of metal extracted the more hydrogen ions would be produced. This result in a decrease in pH of the system and consequently a decrease in the amount of metals extracted (the reverse reaction in Equation 4.1).

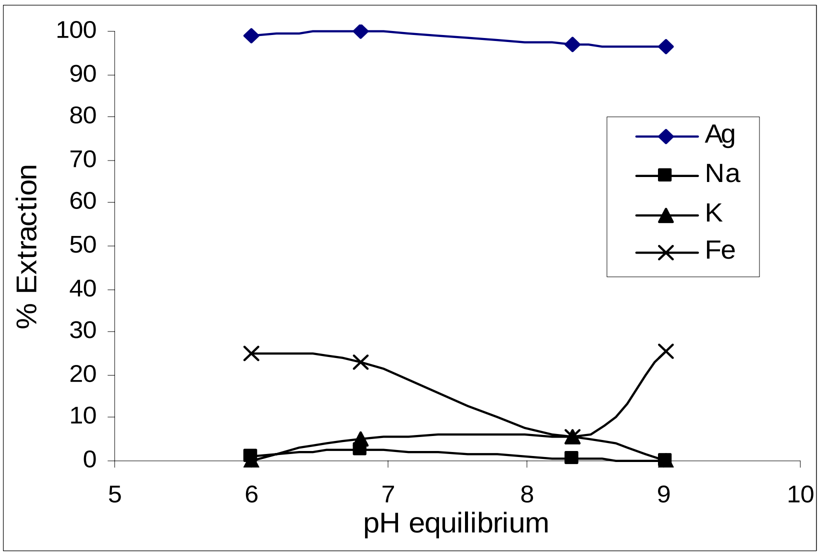


Figure 4.3: Metal extraction from liquid photographic waste (Experimental Conditions: [Carrier] = 0.05 M, agitation speed = 250 rpm, T = 26 ºC).

Figure 4.3 shows the extraction performance of Cyanex 302 at various pH systems. The maximum percentage of iron, sodium and potassium is less than 25% while the extraction of silver is around 97 %. This means that the Cyanex 302 is selective towards silver at pH equilibrium range understudied. This might be due to the fact that the Cyanex 302 has higher acidic properties and it is more soluble in water. Sulfur substitution causes this extractant acidity to increase, making them particularly suitable for the extraction of soft lewis acid metal ions such as Ag(I), Ni(II), Zn(II), Cu(I), Au(I) and platinum group metals which are in accordance with the HSAB principle (Pearson, 1963). Therefore, reagents containing a sulfur donor atom are expected to be suitable extractants for soft metal ions such as silver.

On the other hand, at low pH values, it is expected that the extraction will decrease due to protonation of the extractant and at high pH values also decrease as a result of hydrolysis of the metal as shown in Figure 4.4 of general effect on pH (Ritcey and Ashbrook, 1984). However, this generalization does not hold for ion-association or solvating extractants because these are not primarily dependent on pH for metal-extractant complex formation, but rather on factors such as anion concentration in the aqueous phase.

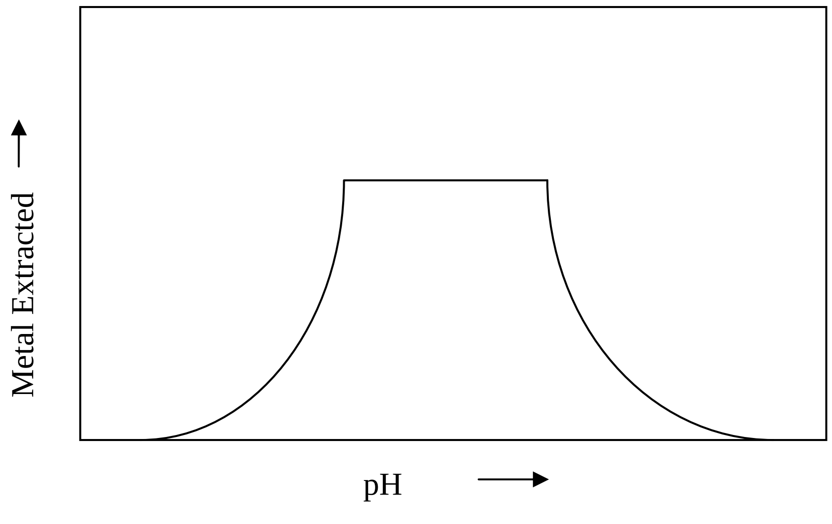


Figure 4.4: General effect of pH on metal extraction (Ritcey and Ashbrook, 1984).

In addition, Cyanex 302 [bis(2,4,4-trimethylpentyl) monothiophosphinic acid] as the respective monothio analog of the commercial reagent, Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid] are accepted as a monobasic organophosphorus acid extractant and dimeric in solvents of low polarity. The dimer arises from strong intermolecular hydrogen bonding. Vapour-pressure osmometry measurements have shown that Cyanex 302 exists predominantly as dimeric species (Tait, 1993). The structure of Cyanex 302 is as illustrated in Figure 4.1.

As an acidic extractant, Cyanex 302 extracts metals by a cation-exchange mechanism, in which hydrogen atoms in the extractant are exchanged with metal ions (Ritcey and Ashbrook, 1984). In the case of photographic wastes, the metal of interest in the solution is silver thiosulfate [$Ag(S_2O_3)_2^{3-}$]. Silver thiosulfate is a very stable complex which is soluble in an aqueous phase, and shows lipophobic characteristic towards an organic phase. The dimeric molecules of Cyanex 302 will associate with the Ag ion from silver thiosulfate, and subsequently render the complex formed lipophilic.

The nature of the extracted species was evaluated by the plot of log D versus log [Cyanex 302] using simulated silver thiosulfate. The slope of the line is equal to the number of molecules of extractant associated with a metal atom in the extracted species. Figure 4.5 shows the result of extraction stoichiometry for Cyanex 302. The slope obtained from the plot was 0.82, which is nearly equal to 1.0. Hence the metal to reagent ratio was found to be 1:1. However, since the photographic waste is a very complicated solution, there is some uncertainty as to the types of extracted species associated with Cyanex 302. There are other types of silver ions in the solution besides silver thiosulfate. Hence, this result does not necessarily apply for a system containing complicated compound like photographic waste. Therefore, the assumption was made that only silver thiosulfate reacted with Cyanex 302.

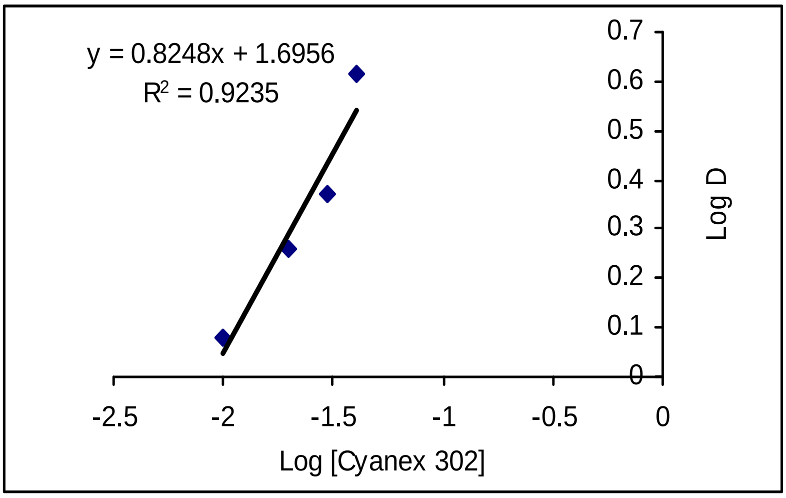


Figure 4.5: Relationship between log D and log [Cyanex 302].

Based on the results from the present experimental work, considering only the silver thiosulfate $Ag(S_2O_3)_2^{3-}$, the extraction of silver is given by the following equation:

$$Ag\left(S_2O_3\right)_2^{3-} + \overline{\left(RH\right)_2} \leftrightarrow \overline{Ag(RH)R} + 2\left(S_2O_3\right)^{2-} + H^{+} \qquad (4.4)$$

Figure 4.6 shows the effect of extractant concentration on the percentage of metal extraction. The percentage of silver extraction increases with increasing extractant concentration until it achieves a plateau, which indicates the excess of ‘free extractant’. At this region, the percentage of silver extraction is almost 100%. For other metals, the percentage of extraction is almost independent on the extractant concentration. It was observed that at very low extractant concentration, metal precipitates, which might be due to the limitation of extractant in the system in order to form metal-extractant complex that is soluble in the organic phase.

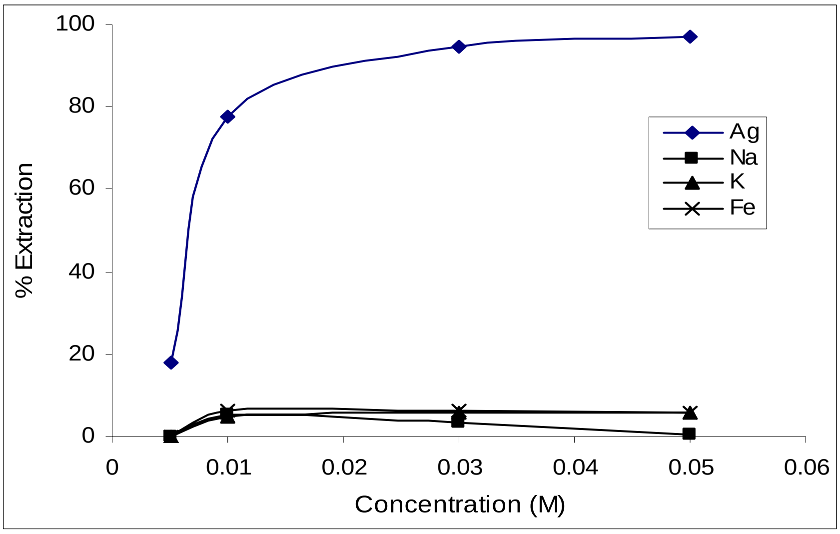


Figure 4.6: Effect of extractant concentration on metal extraction from photographic wastes without pH adjustment using Cyanex 302 (Experimental conditions: A/O ratio = 1:1, agitation speed = 250 rpm, and T = 26 °C).

As reported by Ritcey and Ashbrook (1984), extraction of a metal by a particular solvent does not necessarily increase linearly with increase in the extractant concentration in the solvent. The deviation from linearity may be due to the dimer formation or polymerization of the extractant or a decrease in solubility of the extractable metal complex without the formation of the third phase. If poor solubility of the extracted species leads to the third phase formation between the diluents and the aqueous phase, a modifier should be added to the solvent to increase the solubility of the extracted species. However, this phenomenon did not occurred in the present system.

4.3.2 Tetramethylthiuram disulfide (Thiuram)

Thiuram is a chelating extractant that contains sulfur donor groups which are capable of forming bidentate complexes with metal ions. The possible extraction mechanism involves the reduction of Thiuram in the presence of thiosulfate ions, followed by chelation of the silver(I) with the reduced Thiuram. Thiuram is reduced to two dithiocarbamate ions in the presence of silver(I) ions, leading to the stable formation of tetrathionate ions and a silver N,N-dimethyldithiocarbamate complex.

The silver(I) ion would be readily extracted with a dithiocarbamate. It is well known that N,N-diethyldithio-carbamate forms complexes with many metal ions as a non selective complexing agent (Thorn and Ludwig, 1962). On the other hand, Mendoza *et al*. (1996) reported that thiuram disulfides have a capability to extract silver from thiosulfate medium. These findings indicate that Thiuram acts as a selective extractant towards silver from original sample of real photographic wastes solution.

Figure 4.7 shows the effect of equilibrium pH on metal extraction using tetramethylthiuram disulfide. The extraction of silver is found to be very selective in the pH range from 8 to 10. The extraction of silver decreases at a low pH because the extractant is unable to ionize as a result of higher concentration of hydrogen ion, therefore, it will not be able to form a complex with a metal ion. Hence, at higher pH the extraction will not occur due to the formation of non-extractable Ag(OH) by hydrolysis of silver ion as reported by Mendoza and Kamata (1996). Thus, it is proposed that the extraction of silver using Thiuram should be conducted in the moderate level of pH values. The extractability of silver is dependent on the concentration of thiosulfate (Mendoza and Kamata, 1996).

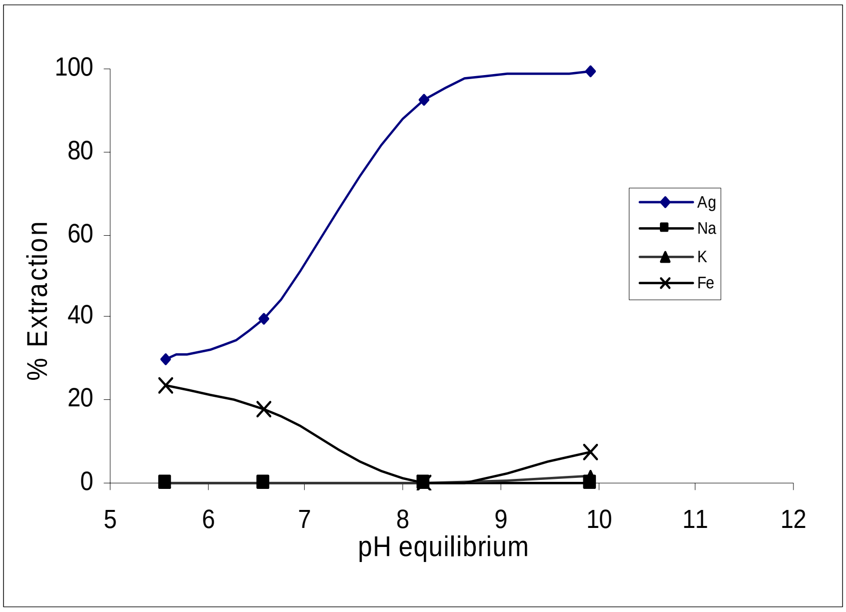


Figure 4.7: Percentage of metal extraction using 0.03 M tetramethylthiuram disulfide in chloroform (Experimental conditions: A/O ratio = 1:1, agitation speed = 250 rpm, and T = 26 °C).

According to the metal ion selectivity, thiuram sulfides which contain two moieties of dithiocarbamates would be expected to exhibit an enhanced selectivity toward metal ions due to the appropriate positions of the two ditiocarbamate groups. The structure of tetramethylthiuram disulfide (Thiuram) is illustrated in Figure 4.8:

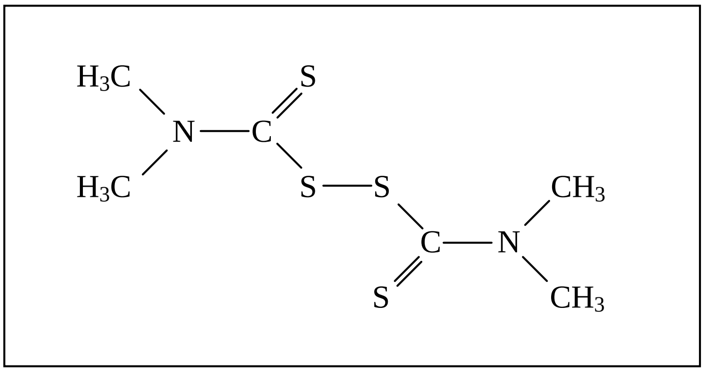


Figure 4.8: A chemical structure of tetramethylthiuram disulfide (Thiuram).

Furthermore, TMTDS having a disulfide bond also possesses extensive resonance stability to silver selectivity. It also contains two moieties of dithiocarbamates that will enhance the silver selectivity due to the appropriate positions of their two dithiocarbamate groups. However, other metal ions in small amounts are also co-extracted as well as silver ions by TMTDS as shown in Figure 4.8 because the C-N bond in the dithiocarbamate has a polar character which enhances the reactivity of the dithiocarbamate molecule (Mendoza *et al.*, 1996).

The extractability of silver with Thiuram can be explained by the size recognition of the ligand to the silver ion (ring size effect). Thiuram possesses the ideal C-shaped cavity to fit the Ag^+, thus the selectivity for Ag^+ is high. The disulfide bond in the molecule of Thiuram also possesses extensive resonance stability. On the other hand, the C-N bond in the dithiocarbamate structure has a polar characteristic, which enhances the reactivity of the dithiocarbamate molecule. Thus it may explain further why other metal ions in small amounts are co-extracted with Ag^+ by Thiuram (Mendoza and Kamata, 1996).

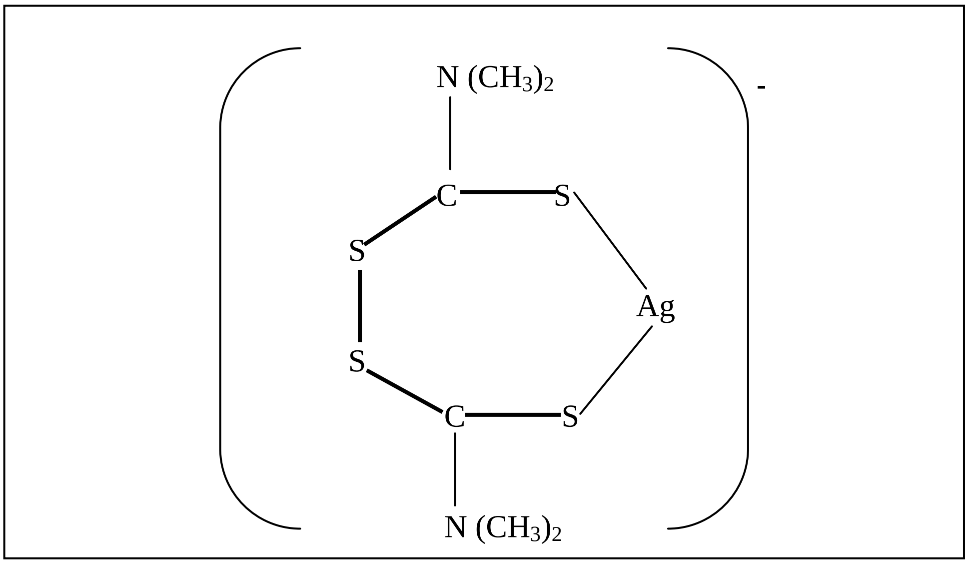


Figure 4.9: A postulated structure of silver complex with TMTDS (C-shaped cavity).

Figure 4.7, also shows that at low pH, the co-extractions of sodium, potassium and iron are very pronounced. These metals compete with silver to associate with Thiuram in an acidic and an alkaline system. This appreciable co-extraction of metals decreased when the extraction process is carried out to the original sample without any chemical adjustment.

The nature of the extracted species was evaluated by the plot of log D versus log[tetramethylthiuram disulfide], by assuming that all the tetramethylthiuram disulfide that existed in the system reacted with silver while percentages of extraction of other metals are negligible. The slope obtained for the plot is 1.1 which is nearly equal to 1.0 (Figure 4.10). Hence the metal to reagent ratio was found to be 1:1. Therefore, it can conclude that one mole of silver reacts with one mole of tetrametylthiuram disulfide, according to equation (1) as presented by Mendoza and Kamata (1996).

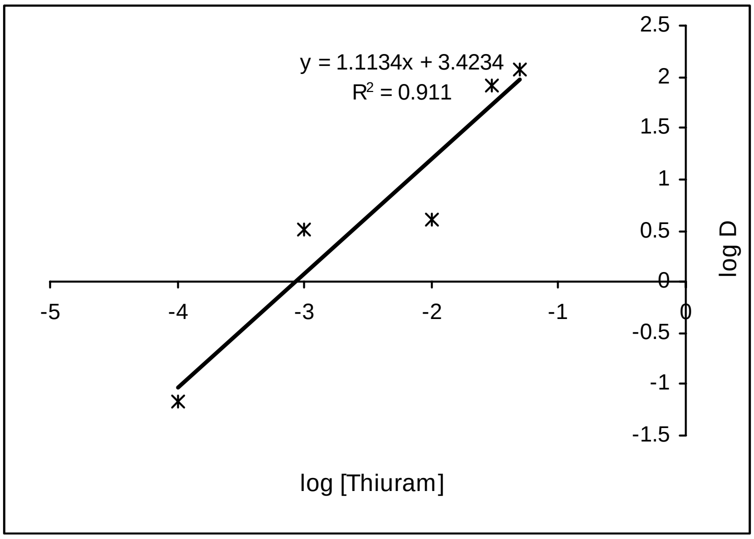


Figure 4.10: A relationship between log D and log [tetramethylthiuram disulfide].

The following reaction explains the extraction mechanism of silver(I) with Thiuram:

$$\begin{aligned}&(CH_3)_2NCS_2S_2CN(CH_3)_2 + Ag(S_2O_3)_2^{3-} \leftrightarrow \\ &\qquad [(CH_3)_2NCS_2 - Ag - S_2CN(CH_3)_2]^- + S_4O_6^{2-}\end{aligned} \tag{4.5}$$

Figure 4.11 shows the percentage of metal extraction, which increases as the extractant concentration increased. The extraction of silver drastically increases with concentration up to 0.03 M, but above 0.03 M, the silver extraction starts to achieve a plateau due to the excess of ‘free’ extractant. It was also found that at a concentration lower than 0.03 M; the extent of silver extraction depends strongly on the extractant concentration. However the extraction may be interfered by other species than silver and thiosulfate ions which delayed the transfer of silver into the organic phase to form the Ag(I)-tetramethylthiuram disulfide complex. (Mendoza and Kamata, 1996).

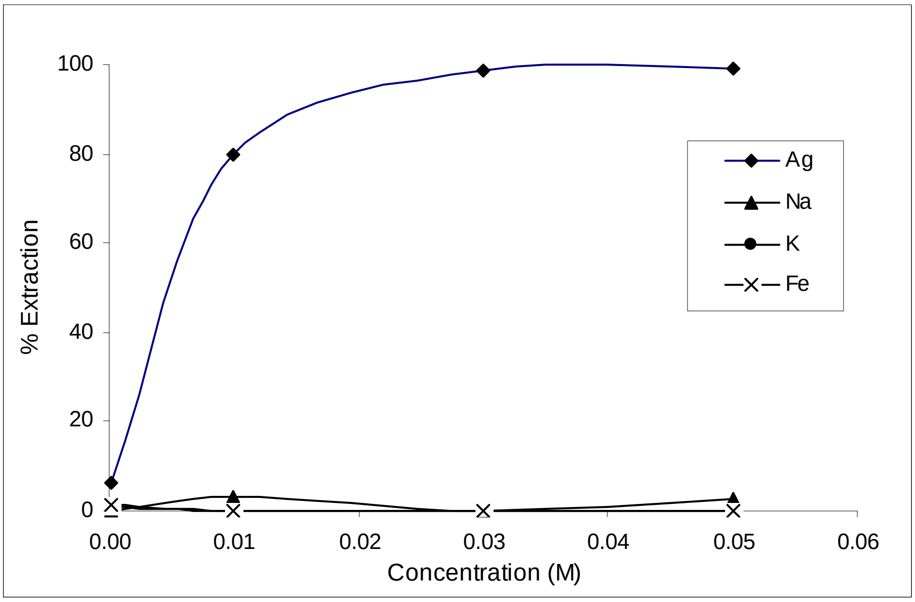


Figure 4.11: Effect of extractant concentration of metal extraction from photographic waste without pH adjustment using tetramethylthiuram disulfide in chloroform (Experimental conditions: A/O ratio = 1:1, agitation speed = 250 rpm, and T = 27 ^{o}C).

4.4 Stripping Selection and Screening

Stripping agent is a very important factor in liquid membrane formulation. It depends on extractant type because some extractants form very stable silver complexes which are very difficult to strip off. As discussed in Section 4.3, a few types of extractant show a good capability in extracting silver from photographic wastes. Cyanex 302 and tetramethylthiuram disulfide were chosen to study the stripping agent type for the metal loaded organic phases.

4.4.1 Metal Loaded Cyanex 302

Several inorganic acids at various concentrations were tested as a stripping agent for the silver recovery from the metal loaded organic phase (Table 4.7). It was found that nitric acid has a good capability to strip silver from metal loaded Cyanex 302. However nitric acid was not recommended as a receiving phase in the emulsion liquid membrane because it tends to destroy and break-up the emulsion. On the other hand, using hydrochloric acid, precipitation of silver chloride occurred at the oil-water interface. It leads to poor stripping percentage in the aqueous phase whiles sulfuric acid is not pronounced as a stripping agent. In addition, acidic thiourea was also tried to use as a stripping agent and was found to have a very good potential as a stripping agent as reported in Table 4.8.

Table 4.7: Effect of Acid types and concentration on stripping of silver from loaded Cyanex 302 organic phase.

Acid Type	[Acid] (Molar)	Initial conc. metal loaded (ppm)	Stripped (ppm)	% S
H_2SO_4	2.00	1583.50	0.03	0.00
	4.00	1583.50	0.05	0.00
	6.00	1583.50	0.10	0.01
HCl	2.00	2739.47	63.55	2.32
	4.00	2739.47	112.15	4.09
	6.00	2739.47	212.82	7.77
HNO_3	2.00	2764.44	17.28	0.63
	4.00	2764.44	343.43	12.42
	6.00	2764.44	789.14	28.55

Table 4.8: Percentage of silver stripping by 0.5 M thiourea in different acid medium at various concentrations (Experimental conditions: A/O ratio = 1:1, agitation speed = 250 rpm, and T = 27 ºC).

Acid concentration (M)	% silver stripping		
	H_2SO_4	HNO_3	HCl
0.0	0.0	0.0	0.0
0.3	100.0	88.5	100.0
0.5	100.0	62.6	100.0
1.0	100.0	40.0	71.1

Furthermore, as reported in several papers, thiourea is an excellent leaching reagent for precious metals (Akretche *et al.*, 1997); in acidic medium (in low pH values) and high concentration, thiourea forms cationic species; they are also extracted by ligands like crown ethers so competition between thiourea and the ligand in metal ion transport is observed. Thiourea ($CS(NH_2)_2$) is capable of forming coordinate bonds through both sulphur and nitrogen atoms even though the extremely low basicity of the ligand plays against the formation of nitrogen-metal bonds. In acidic medium, thiourea is protonated and the proton will be bonded to the sulfide atom favouring the bonding of the metal ions to nitrogen atoms. However, the pH of thiourea solutions is a fundamental parameter for the formation of gold-thiourea complex and its stability (Gherrou and Kerdjoudj, 2002).

The stripping reaction of silver(I) complex with acidic thiourea is proposed below:

$$\overline{Ag(RH)R} + CS(NH_2)_2H^+ \leftrightarrow \overline{(RH)_2} + Ag(CS(NH_2)_2)^+ \qquad (4.6)$$

In order to determine the most suitable acid solution of thiourea, the performances of silver stripping using 0.5 M thiourea in three different types of acids such as H_2SO_4, HCl and HNO_3 were studied. The result as shown in Table 4.8 indicates that H_2SO_4 exhibits better performance in stripping silver from loaded organic phase at concentration range understudied while the performance of HCl and HNO_3 decreased as the molarities of the acids increased. On the other hand, a pure thiourea solution does not act as a stripping agent of silver from Cyanex 302-silver complexes.

The performance of thiourea to strip silver from the organic phase at varying concentrations is presented in Table 4.8. The result shows that thiourea in H_2SO_4 provides an excellent stripping percentage which is nearly completed even at concentration of 0.3 M acid. Further increment of thiourea concentration to 0.5 M has only slight enhancement on the degree of stripping.

On the other hand, when the concentration of HNO_3 and HCl acids increased to 1.0 M, the stripping performance quantitatively decreased. Therefore, even though thiourea functions well as a stripping agent in the acidic solution, there seem to be a limitation on the extent of acidity of the solution. If the acidity of the solution is high, more thiourea is needed to ensure that the acidic thiourea acts as an excellent stripping agent for Cyanex 302. As shown in Table 4.9, at a fixed concentration of the acid solution, increasing thiourea concentration will increase the percentage of silver extraction. The results suggest that the molar ratio of thiourea to acid concentration must be at least one to one ratio.

Table 4.9: Percentage of silver stripping at various concentrations of thiourea (Experimental conditions: A/O ratio = 1:1, agitation speed = 250 rpm, and T = 27 ^{o}C).

[Thiourea], (M)	Acid			
	[H_2SO_4], M	% Ag Stripping	[HCl], M	% Ag Stripping
0.3	0.3	99.6	1.0	15.7
0.5		100.0		71.1
1.0		100.0		100.0

In the selectivity, acidic thiourea is very selective to silver as shown in Figure 4.12. The amount of other metals being stripped is not appreciable and can be neglected at all thiourea concentration under studied.

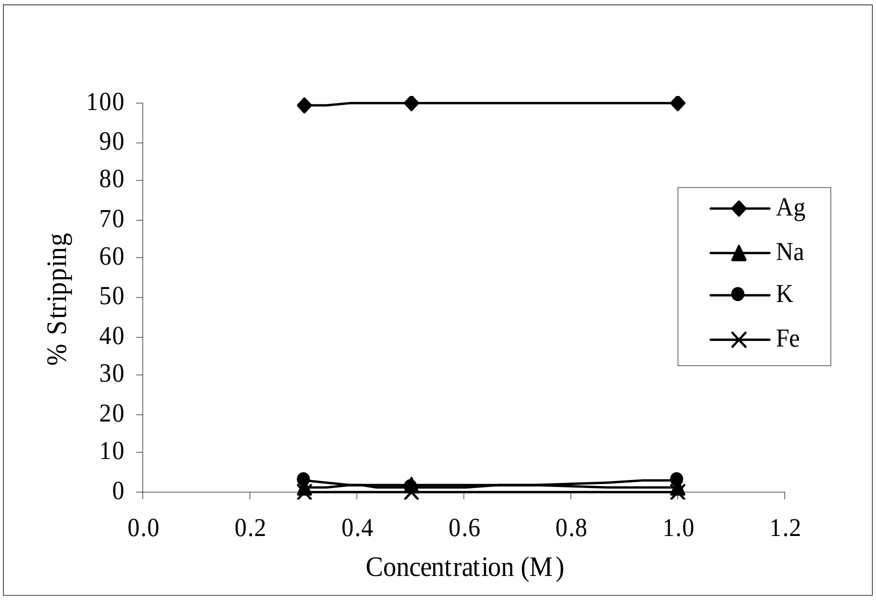


Figure 4.12: Effect of thiourea concentration in 0.3 M H_2SO_4 on stripping of silver from loaded Cyanex 302 organic phase.

4.4.2 Metal Loaded Tetramethylthiuram Disulfide

Table 4.10 shows the results on the effect of acid types and concentration on silver stripping from metal loaded organic solution. It was found that silver stripping using sulfuric acid was not successful in significant amount for metal loaded organic phase even at high concentration (6 M). It means that sulfuric acid is not suitable as a stripping agent for this metal loaded organic phase. However the percentage of silver stripping increased when using high concentration of hydrochloric and nitric acids concentration. The percentage of silver being stripped is around 40% and 68% at 6 M acid concentration respectively. On the other hand, increasing the molarities of HCl or HNO_3 is not advisable, even though it increases the efficiency of the silver stripping from the organic phase, because it hastens the decomposition of the extractant.

Table 4.10: Effect of acid types and concentration on stripping of silver from loaded tetramethylthiuram disulfide organic phase – photographic wastes.

Acid Type	[Acid] (Molar)	Initial conc. metal loaded (ppm)	Stripped (ppm)	% S
H_2SO_4	2.00	1915	1.54	0.08
	4.00	1915	0.06	0.00
	6.00	1915	0.99	0.05
HCl	2.00	1915	8.02	0.42
	4.00	1915	102	5.31
	6.00	1915	747	39.04
HNO_3	2.00	1973	1040	52.77
	4.00	1915	1560	81.42
	6.00	1915	1310	68.50

From the results presented, HNO_3 appeared to show better performance in stripping compared to HCl. However, when considering the reactions of stripping for HCl and HNO_3 respectively, it is noticed that the reaction between silver(I) complex with HCl (Equation 4.7) will form insoluble silver chloride (AgCl) at a low concentration of acid solution, which is not detectable by AAS. Silver will only become soluble when the concentration of acid solution is sufficiently high. Therefore, it is not conclusive that HCl in a low concentration, for example 2M, is not capable of stripping silver from the organic phase. It might happen that the stripped silver exists in the form of insoluble silver chloride (AgCl) which is not detectable by AAS. In contrast, at high concentration of HCl, as high as 6 M, some of the silver change into soluble silver dichloride ($AgCl_2^-$) which is detectable by AAS. As a result, the degree of stripping at this concentration appears to be higher than that at the lower concentrations.

On the other hand, the reaction between silver(I) complex with HNO_3 (Equation 4.8) does not have the same problem as HCl. Silver(I) complex reacts with HNO_3 to form soluble silver nitrate, which can be detected by AAS from the aqueous phase. The result shows 80% of silver was stripped from metal loaded

Thiuram. However, at 6 M concentration the extractant will be destroyed by the acids and consequencely the stripping degree will decrease from 81 % to 68%.

The mechanism involved when silver(I) complex reacts with HCl is shown in the following equation (Mendoza and Kamata, 1996):

$$\begin{aligned}&\left[(CH_3)_2NCS_2-Ag-S_2CN(CH_3)_2\right]^- + 2HCl \leftrightarrow\\&\qquad AgCl_2{}^- + 2(CH_3)_2NCS_2{}^- + 2H^+\end{aligned} \tag{4.7}$$

As for HNO_3, the reaction is as follows:

$$\begin{aligned}&\left[(CH_3)_2NCS_2-Ag-S_2CN(CH_3)_2\right]^- + 2HNO_3 \leftrightarrow\\&\qquad Ag(NO_3)_2{}^- + 2(CH_3)_2NCS_2{}^- + 2H^+\end{aligned} \tag{4.8}$$

Beside of the strength of acids, the chemical complexity of photographic wastes becomes one of the main factors in determining the success of the silver stripping process. It is due to various complex formed was soluble in organic phase and might interfere the silver stripping process.

Another promising stripping agent is acidic thiourea. The metal loaded organic phase is shaking with the stripping agent for 18 hours. The organic phase will allocate below the aqueous phase because its density is higher than the aqueous phase. Initially the organic phase is either grey in color or turbid, depending on the concentration of Thiuram. After stripping, the organic phase shows changes in color and becomes light yellow.

Thiourea at various concentrations in 0.3 M H_2SO_4 and 1.0 M HCl was used to strip silver from the loaded organic phase as shown in Table 4.11. The results obtained show that 30% of silver was stripped out at thiourea concentration range under studied. On the other hand, thiourea in 1.0 M HCl shows the percentage of stripping increases when the concentration of thiourea in the acidic solution increased.

Table 4.11: A comparison of stripping agents for metal loaded Thiuram (Experimental conditions: A/O ratio = 1:1, agitation speed = 250 rpm, and T = 27 ºC).

Concentration of thiourea	Acid			
	H_2SO_4	% Ag Stripping	HCl	% Ag Stripping
0.3M	0.3M	31.1	1.0M	29.0
0.5M		29.3		72.1
1.0M		27.8		100.0

The possible reaction of stripping between silver(I) complex with acidic thiourea is as follows:

$$\begin{aligned}&\left[(CH_3)_2NCS_2 - Ag - S_2CN(CH_3)_2\right]^- + 2CS(NH_2)_2H^+ \leftrightarrow \\ &\qquad 2(CH_3)_2NCS_2{}^- + 2NH_4{}^+ + Ag(SCN)_2{}^- + 2H^+\end{aligned} \tag{4.9}$$

4.5 Emulsion Liquid Membrane and Stability

The selection of the liquid membrane components in the emulsion liquid membrane system is important for selectivity, capacity and stability. The factors such as the membrane solvent, surfactant concentration, and the internal droplet size distribution are crucial to membrane stability for perfect separation and extraction efficiency of emulsion liquid membrane systems.

The main factor influencing the emulsion stability is the types of surfactant or emulsifier. Emulsifier is a surface-active compound that adsorbs at the interface to lower interfacial tension to produce a physical resistance to coalescence and occasionally to increase the surface charge. However the solubility of emulsifiers in water generally follows their HLB rank. As a rule, emulsifiers with HLB values in the range 3-6 promote W/O emulsions while values 8-18 promote O/W emulsions.

Therefore in this study sorbitan monooleate (SPAN 80) with HLB 4.3 was used as the W/O emulsifier.

The stability of the emulsion depends on several factors such as interfacial tension and repulsion by an electric charge. Despite lowering of interfacial tension when the surface active agents are added, the free energy of the interface remains positive, leaving a persisting state of thermodynamic instability. Another factor is repulsion by electric charge which is according to the DLVO (Double layer repulsion and van der waals attraction) theory, the dispersed particles are subjected to two independent forces: the van der waals force of attraction and the electrostatic force of repulsion arising from the presence of the electrical double-layers at the particle surfaces. The net interaction between the particles is obtained by summing these two terms. If the repulsion potential exceeds the attraction potential, an energy barrier opposing collision results and if the magnitude of this energy barrier exceeds the kinetic energy of the particles, the suspension is stable. This means coalescence usually occurs when a drop approaches a fluid-fluid interface, where an interfacial film forms, drains to certain thickness, and then ruptures. A significant distribution of coalescence times is often observed, which may be attributed to the random nature of the disturbances which cause the film to thin and break such as vibration corrugation at the interface, thermal, velocity and interfacial tensions gradients (Lang and Wilkie, 1971). On the other hand, Ivan and Peter (1997) reported the particle collisions will result in coalescence process, flocculation, or particle rebound as a stable emulsion as shown in Figure 4.13.

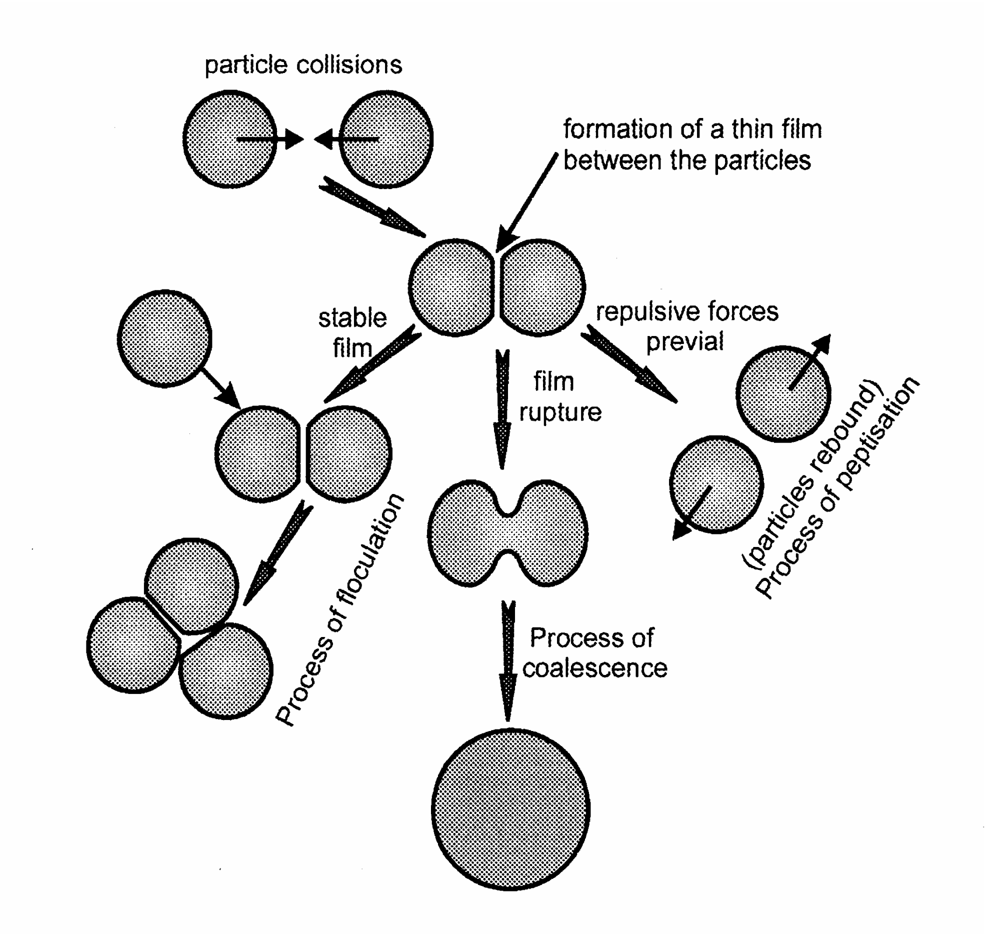
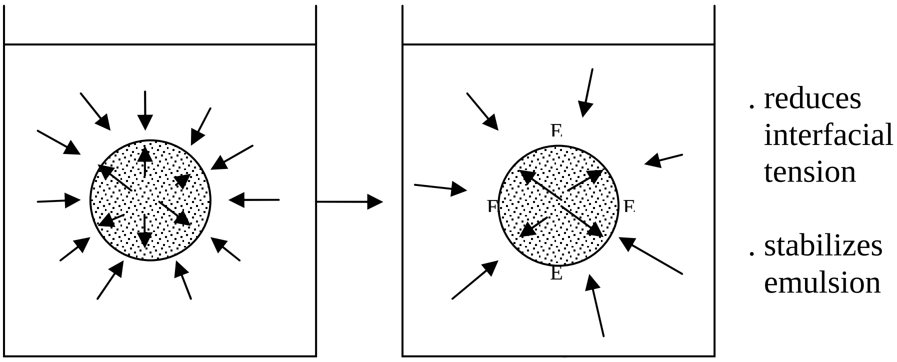


Figure 4.13: Possible result of the collision of two emulsion droplets in connection with the droplet-droplet interaction (Ivan and Peter, 1997).

4.5.1 Effect of Surfactant Concentration

Surfactant concentration is one of the most important factors influencing the stability of emulsions. Several investigations have demonstrated that the emulsifier concentration can strongly influence the emulsion stability (Ostberg *et al.*, 1995). It was observed that there existed a concentration window, out of which the stability quickly deteriorated. It is also reported that the primary driving force for the phase separation is droplet interfacial free energy (Sjoblom, 1996). Therefore, surfactant which concentrates at the oil-water interface imparts a degree of stability to the system by lowering interfacial tension as shown in Figure 4.14. In addition, reduction in interfacial tension facilitates emulsion formation and prevents immediate droplet re-coalescence during preparation. However, for obtaining long-term emulsion stability, the strength of the interfacial film formed by a surfactant has been reported to be more important than its effect on interfacial tension (Sjoblom, 1996; Myers, 1988). Tables 4.12 and 4.13 show the stability test for both carriers of Cyanex 302 and Thiuram at various surfactant concentrations. Emulsion stability was gauged by measuring the water and oil resolved from the emulsion as a function of time. Table 4.12 shows 3% (w/v) Span 80 is enough to form stable emulsion, increasing its concentration from 5% to 7% does not make any large difference in water/oil separation except at the initial stage of separation, where the rate of oil separation is high for 3% compared with the other concentrations.

The result also shows that the stability of emulsion increased with increasing surfactant concentration. At low surfactant concentration, the emulsion is not stable due to agglomeration of the water droplets; at high surfactant concentrations, emulsion destabilization occurs as a result of rapid coalescence. This finding is agreement with the works of Ivan and Peter (1997), on the effect of surfactant concentration.



Addition of emulsifier (E) to the liquid/liquid interface

Figure 4.14: Effect of emulsifier at liquid/liquid interface (Ivan and Peter, 1997).

Table 4.12: Effect of surfactant concentration on emulsion stability (Experimental conditions: [Cyanex 302] = (0.05 M), homogenizer speed = 13500 rpm, mixing time = 5 min, stripping phase = 1.0 M thiourea in 1.0 M H_2SO_4, and temperature = 26 ºC).

[Span 80] / Day	3%		5%		7%	
	Oil	Water	Oil	Water	Oil	Water
1	1.0	0.0	1.0	0.0	1.0	0.0
2	1.7	0.0	1.5	0.0	1.5	0.0
3	2.0	0.0	2.0	0.0	1.8	0.0
4	2.4	0.0	2.4	0.0	2.0	0.0
5	2.5	0.0	2.5	0.0	2.2	0.0
6	2.7	0.4	2.7	0.0	2.4	0.0
7	2.8	0.7	2.8	0.0	2.5	0.0
8	3.0	1.5	2.9	0.0	2.7	0.0
9	3.3	2.3	3.0	0.3	2.7	0.0
10	3.5	2.5	3.1	0.7	2.8	0.0
11	3.9	3.0	3.2	1.5	3.0	0.0
12	4.1	3.3	3.3	2.3	3.0	0.1
13	4.3	3.5	3.6	2.6	3.0	0.5

Table 4.13: Emulsion stability of Thiuram (0.03 M) in Chloroform (Experimental conditions: homogenizer speed = 13500 rpm, mixing time = 5 min, stripping phase = 1.0 M thiourea in 1.0 M HCl, and temperature = 26 ºC).

[Span 80] / Day	3% (w/v)		5% (w/v)		7% (w/v)	
	Oil	Water	Oil	Water	Oil	Water
1	5.0	3.5	3.5	0.0	3.0	0.0
2	5.0	4.0	4.0	0.0	3.5	0.0
3	5.0	4.3	4.2	0.0	4.0	0.0
4	5.0	4.5	4.5	0.5	4.2	0.5
5	5.0	5.0	4.3	1.0	4.3	1.0
6	5.0	5.0	4.8	1.5	4.8	1.5
7	5.0	5.0	5.0	3.0	5.0	3.5
8	5.0	5.0	5.0	4.0	5.0	4.5

4.5.2 Effect of Diluents

Diluent plays an important role in making an emulsion liquid membrane. It has been long recognized the importance of the correct diluents choice in extraction processes (Ritcey and Ashbrook, 1984) and since the membrane organic phase consisted of an extractant and a diluents, the role of the diluents on the transport and in the membrane stability becomes most important factor. Table 4.14 shows the physical properties of diluents used in silver extraction from real liquid photographic wastes. Tables 4.15 and 4.16 show the stability of emulsion when using different types of diluents. As shown in Table 4.15, the stability of Cyanex 302 depends strongly on the type of diluents used. Based on the observation, kerosene formed a stable emulsion compared to toluene and n-dodecane. It is due to the long chain (greater than C_{10}) aliphatic hydrocarbons or kerosene type diluents (Draxler and Marr, 1986). The aliphatic hydrocarbons are less hydrophilic than aromatics. The solubility of these solvent in water is typically on the order of one to five parts per million. On the other hand, Table 4.16 indicates that Thiuram in toluene was more stable compared to that of chloroform system. Water solubility of chloroform is higher than toluene and solubility of toluene is higher than kerosene which is make it easy for it to interact with water molecule and this leads to the break down of the emulsion. Another factor is the rate of water/oil separation of chloroform is faster than that of the toluene system.

Table 4.14: Physical properties of diluents used in silver extraction process.

Organic diluent	Viscosity (μ) at 25ºC (cP)	Density at 25ºC (kg.m^{-3})
Kerosene	2.20	0.78
Toluene	0.68	0.87
Chloroform	0.38	1.49
n-Dodecane	1.34	0.75

Another factor influencing membrane stability is viscosity of liquid membrane. Table 4.14 shows the viscosity of diluents used in liquid membrane formulation. High viscosity diluents form more stable emulsion. Table 4.15

indicates that Cyanex 302-kerosene type liquid membrane is more stable than toluene and dodecane while the thiuram-toluene type liquid membrane is more stable than chloroform.

Table 4.15: Emulsion stability of Cyanex 302 (0.05 M) in different diluents (Experimental conditions: homogenizer speed = 13500 rpm, mixing time = 5 min, stripping phase = 1.0 M thiourea in 1.0 M H_2SO_4, Span 80 = 5%, and temperature = 26 ^oC).

Diluent / Day	Kerosene		Toluene		n-Dodecane	
	Oil	Water	Oil	Water	Oil	Water
1	0.9	0.0	2.2	0.0	1.2	0.0
2	2.2	0.0	2.8	0.0	2.4	0.0
3	2.4	0.0	3.0	0.0	2.8	0.0
4	3.0	0.0	3.2	0.0	2.9	0.0
5	3.1	0.0	3.3	0.1	3.0	0.0
6	3.3	0.5	3.5	0.2	3.2	0.0
7	4.0	1.0	4.2	1.0	3.8	0.7

Table 4.16: Emulsion stability of Thiuram (0.05 M) in different diluents (Experimental conditions: homogenizer speed = 13500 rpm, mixing time = 5 min, stripping phase = 1.0 M thiourea in 1.0 M HCl, Span 80 = 5% (w/v), and temperature = 26 ^oC).

Diluents / Day	Toluene		Chloroform	
	Oil	Water	Oil	Water
1	2.0	0.0	3.5	0.0
2	2.5	0.0	4.0	0.0
3	2.5	0.0	4.2	0.0
4	2.7	0.0	4.5	0.5
5	3.0	0.0	4.3	1.0
6	3.0	0.0	4.8	1.5
7	3.1	0.0	5.0	3.0
8	3.2	0.0	5.0	4.0

4.5.3 Effect of Homogenizer Speed

There are many different ways of preparing emulsions of two liquids that are insoluble. Emulsification is usually achieved by the application of mechanical energy. Initially, the interface between the two phases is deformed to such an extent that large droplets are formed, and these large droplets are subsequently broken up into smaller ones. During emulsification, the interfacial area between two liquids increases. Liquids tend to minimize the surface area and therefore, mechanical energy is required for forming emulsion. Table 4.17 shows the stability test for Cyanex 302 at various homogenizer speed such as 8000, 9500 and 13500 rpm. The result shows that the stability of emulsion increased with increasing mixing speed, where the emulsion formed by 13500 rpm is more stable than 8000 rpm based on water/oil separation in Table 4.17. The stability of emulsion without water droplets breaking is 4 days for 8000 rpm and 6 and 8 days for 9500 rpm and 13500 rpm respectively. This finding is in line with the reports by Lissant (1983) which indicates that the larger the particle, the less distance it travels in any direction due to Brownian effects while small particles have Brownian motion to deflect their already slower settling. His result indeed showed that larger particles settle quickly but smaller particles, due to Brownian displacement, take much longer to settle. In addition, Lissant (1983) also incorporated the effect of Stoke's settling velocity and Brownian motion in modeling the settling of dispersed drops in emulsions as presented in Table 4.18. This result also proved the emulsion stability of higher speed homogenizer which forms smaller emulsion size. The smaller size of emulsion has a lower Stokes Falling and high distance of Brownian movement thus make it difficult to settle.

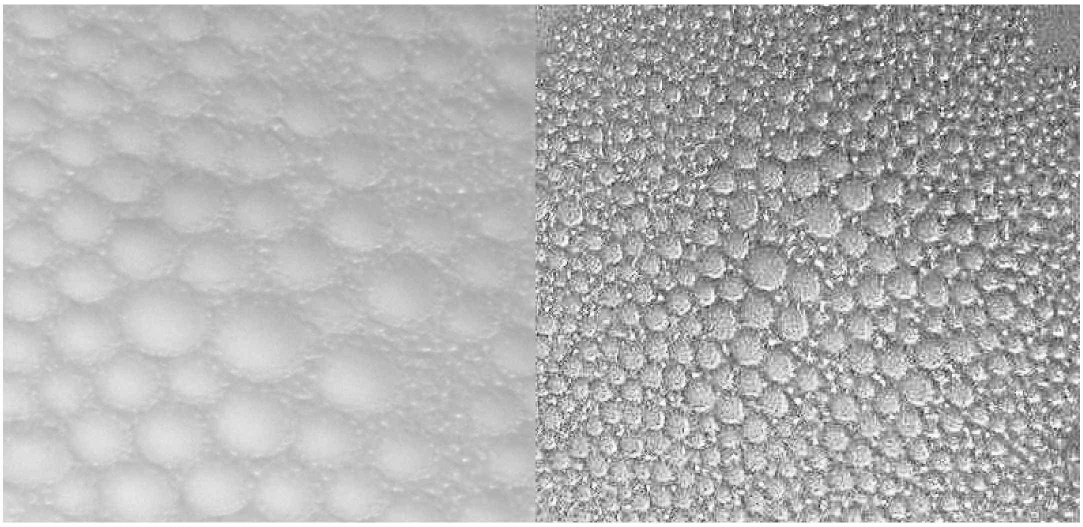
Therefore this argument was in conjunction with this experiment results. Figure 4.15 shows that the size of emulsion droplet of 8000 rpm is larger than 13500 rpm (undetectable because very small size in some cases), makes it easy to settle as the result presented in Table 4.17. This is due to the tendency of droplets to settle and thus be brought into close physical proximity of one another by random motion of particle (Brownian motion).

Table 4.17: Effect of homogenizer speed on W/O emulsion stability of Cyanex 302 (0.05 M) in kerosene (Experimental conditions: stripping phase = 1.0 M thiourea in 1.0 M H_2SO_4, [Span 80] = 3% (w/v), mixing time = 5 min, and temperature = 26 ºC).

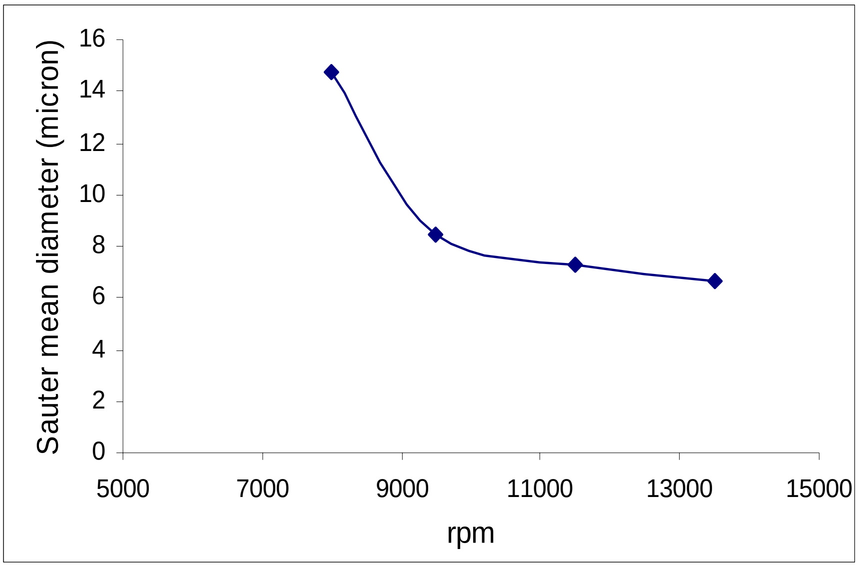
Speed / Day	8000 rpm		9500 rpm		13500 rpm	
	Oil	Water	Oil	Water	Oil	Water
1	2.5	0.00	1.5	0.0	1.0	0.0
2	3.8	0.00	2.5	0.0	1.9	0.0
3	3.8	0.00	2.8	0.0	2.5	0.0
4	3.9	0.01	3.2	0.0	2.8	0.0
5	3.9	0.02	3.3	0.0	2.8	0.0
6	3.9	0.02	3.4	0.3	3.0	0.0
7	4.0	0.02	3.5	0.5	3.1	0.0
8	4.0	0.02	3.5	0.8	3.1	0.1

Table 4.18: Particle movement versus droplet size (Lissant, 1983).

Particle size (μm)	Stokes falling (μm)	Brownian movement (μm)
1	0.7	2.000
5	16.3	0.890
10	65.3	0.632
20	261.3	0.447
30	588.0	0.365
40	1045.3	0.316
50	1633.3	0.283
60	2352.0	0.258
70	3201.3	0.239
80	4181.3	0.224
90	5292.0	0.211
100	6533.3	0.200



(a) 8000 rpm (b) 13500 rpm



(c)

Figure 4.15: Effect of homogenizer speed on size of W/O emulsion (Experimental conditions: [Cyanex 302] = 0.05 M, stripping phase = 1.0 M thiourea in 1.0 M H_2SO_4, [Span 80] = 3% (w/v), mixing time = 5 min, and temperature = 26 ^oC).

4.6 Photographic Waste Characterizations

The physical and chemical characterizations of the photographic wastes were carried out in order to determine the cations and anions compositions, pH, density, and viscosity. These properties, especially those of the cations and anions compositions are important in order to explain silver extraction from photographic wastes. The cations content analyzed are silver, sodium, potassium, iron, copper, zinc, lead, chromium, cadmium, and nickel while the anions are chloride, nitrate, sulfide and fluoride. Table 4.19 shows that the silver, sodium, potassium, and iron exist in high concentration in the photographic wastes and the others metals are less than 1.5 ppm while the anion contents are in the following order: sulfate > nitrate > chloride > fluoride. However, during photo processing, particularly in the fixing or bleach-fix, silver is removed from the film or paper usually in the form of thiosulfate complex (Pro-ACT, 1995).

Table 4.19: Physical and chemical properties of real photographic wastes solution.

Cations	Concentration (ppm)	Anions	Concentration (ppm)
Ag	2490	Cl^-	249
Na	3630	NO_3^-	2200
K	6240	SO_4^{2-}	3710
Fe	1480	F^-	62
Zn	0.38		
Cu	0.17	Physical properties	
Pb	1.36	pH	~7.5- 8.5
Cr	0.29	Density	1.04 g/ml
Cd	0.24	Viscosity	0.77 cP
Ni	0.86		

4.7 Summary

Emulsion liquid membrane component selection is the main study in constructing emulsion liquid membrane process. It involves carrier and strip agent selection to the target metal ions such as silver, and the membrane stability. The carrier must be easy to react with the metal ion to form complexes and miscible in liquid membrane and then ready to release the metal in stripping phase. Therefore, Cyanex 302 and acidic thiourea at certain concentration and conditions was chosen as promising carrier and strip agent of silver from photographic wastes. The main factor in ELM process is emulsion stability. In making stable emulsion a few factors must be considered such as emulsifier types and concentration, diluents, conditions of emulsion making and also experimental conditions during extraction process. When all the criteria are satisfied the possibility of emulsion liquid membrane to extract silver from photographic wastes will be realized.

CHAPTER 5

EMULSION LIQUID MEMBRANE EXTRACTION

5.1 Introduction

Since the advantage of ELM method is potentially very large, it is selected in this study as the separation method for silver from the photographic waste. The principle of ELM process is mass transfer of solute from a waste solution into an internal aqueous phase, suited for an irreversible capture of transported solutions. Thus, the process parameters such as carrier and receiving agent impose the mass transfer direction of the system. Other process parameters that have pronounced effect on the ELM process are the selection of surfactant, treat ratio of emulsion to feed phase, diluents, and agitation speed.

This thesis will explain and highlight the effects of systematic changes in the process parameters of emulsion liquid membrane system performance on silver extraction. These effects were determined through the amount of metal extracted, the net change in the interior phase volume, the swell and breakage experienced by the system. The batch experiment with mixer settler was examined and will be discussed in this chapter. For the initial studies of the emulsion liquid membrane system, the standard formulations listed in Table 5.1 are being used**,** unless otherwise stated.

Table 5.1: Experimental conditions used for the preparation of ELM.

Internal aqueous phase	V_{int} = 10 ml
Organic phase	V_{org} = 10 ml
Solvent	Kerosene
[Carrier]	0.01 M - 0.10 M
[Surfactant]	1 % - 7 % (w/v))
External aqueous phase	100 ml
Treat ratio	(V_m/V_{ext}) 1:3 - 1: 7
Stirring speed	(200 – 350) rpm
Temperature	300 K

As reported in the literature, it is difficult to select the optimal conditions for the ELM extraction process. It is due to many parameters influencing the ELM process. Therefore, in this thesis**,** attention has been focused on the extraction of silver from photographic waste (feed solution) by the ELM technique. Two systems will be studied in this aspect and several parameters such as the metal selectivity, extraction time, level of agitation, surfactant concentration, carrier concentration, acidic level of stripping agent type, type of diluents and treat ratio will be studied in order to discover the factors that influence the extraction performance. The first system that will be covered is the Cyanex 302 in kerosene, which will be the main attention of this study whereas the second system which comprises of TMTDS in toluene will be investigated as comparison over the first system. The performance of the ELM extraction technique was measured by the following terms:

$$\% \text{ E} = \frac{C_{ex,o} - C_{ex,f}}{C_{ex,o}} \text{ x } 100\% \qquad (5.1)$$

or $$\frac{C_{ex,f}}{C_{ex,o}} \text{ (dimensionless form)} \qquad (5.2)$$

$$\text{\% Break-up} = \frac{V_{\text{int},f} - V_{\text{int},o}}{V_{\text{int},o}} \text{ x } 100\% \qquad (5.3)$$

5.2 Batch Emulsion Liquid membrane Extraction – Cyanex 302

5.2.1 Effect of Extraction Time

The extraction time is defined as the mixing time of the three phase W/O/W emulsion system. It is one of the most important parameters in emulsion liquid membrane system. Longer extraction times result in more transfer of water inside the internal phase, which causes the membrane to swell which subsequently initiates breakage of the emulsion phase and cause leakage of solute from the internal phase to the external phase (Kulkarni *et al.*, 2000). Besides, an appropriate extraction time is needed to increase the mass transfer of metal ions from the external phase to the organic membrane phase. Figure 5.1 exhibits the percentage extraction of silver from the external phase as a function of extraction time.

The extraction performance increased when the extraction time is increased and reached maximum extraction at 3 minutes of process time. After 15 minutes, the degree of extraction decreased probably as a result of the breakage of the emulsion phase. This emulsion breakage will cause the leakage of silver from the internal phase to the external phase and therefore, the metal remaining in the external phase increased after 15 minute. Figure 5.1 also shows that the percentage of emulsion breakage increased to 18 % during the extraction process. It is due to many factors such as type of stripping agent, agitation speed, method of emulsion making and many other factors that will be discussed later in this thesis. However, at an initial stage of 15 minutes operation no emulsion breakage was recorded but the emulsion had swollen 12 %. However after 20 minutes, neither emulsion swelling nor breaking was observed, indicated the rate of swelling and emulsion breaking were equal. Then, further extraction will cause emulsion break-up.

For further study, 20 minutes total operation time was selected since the ELM process performed under the typical conditions of Table 5.1 reached equilibrium in this time of period.

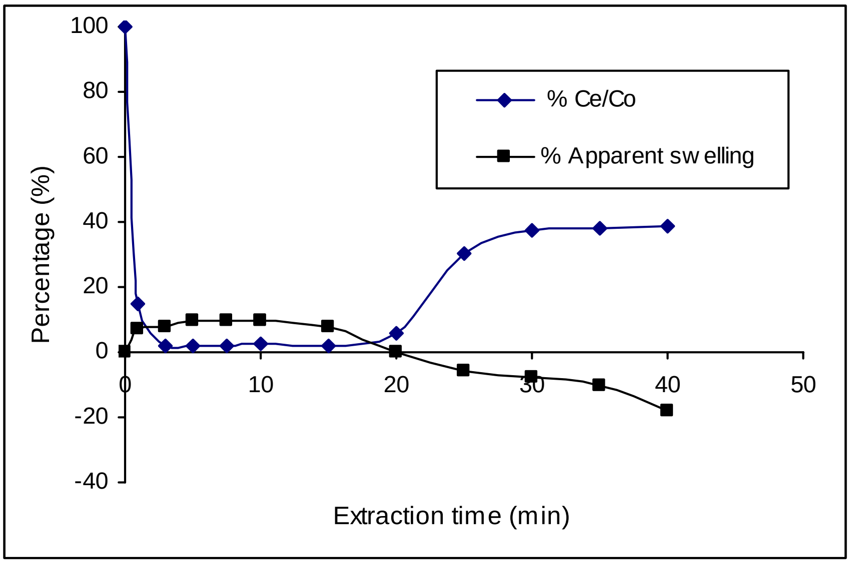


Figure 5.1: Effect of extraction time on the silver extraction (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, speed = 250 rpm, feed phase = real liquid photographic waste, stripping phase= 1 M thiourea in 1 M H_2SO_4; and diluents = kerosene).

5.2.2 Effect of Stripping Agent Types and Concentration

The type of stripping agent plays an important role in silver recovery and minimizing the co-transport of water in the extraction process. Its concentration as well as the internal phase volume fraction cannot be changed or increased indefinitely. If the concentration of the internal reagent is beyond a limiting value, it will be harmful to the stability of the membrane and will increase water permeability in the membrane. This will lead to obvious swelling due to the high osmotic pressure gradient between the internal and external phases. Different types of thiourea solution were tested as a stripping agent of silver from photographic wastes. The result indicated the concentration of thiourea and types of acid used play an important role in obtaining the better emulsion liquid membrane system. Thiourea in H_2SO_4 solution provides better extraction compared to thiourea in HCl and HNO_3 solution. Silver is completely extracted using 1.0 M thiourea in the H_2SO_4 solution as shown in Table 5.2. The result also shows that by decreasing thiourea concentration, the silver extraction also decreased. Similar effect was found when lowering the acid solution concentration.

To study the experience of using different types of acid solution during the ELM process, a few experiments were carried out. Figure 5.2 shows the silver extraction performance using 1.0 M Thiourea in 1.0 M H_2SO_4 and HCl acid solution. The result shows that the extraction rate using the sulfuric acid solution system is more momentous than that using the hydrochloric acid solution especially at the initial stage of the process. It is due to high hydrogen ion gradient at the initial stage acting as a driving force. The flux gradually decreased as the driving force decreased until the maximum extraction was achieved. At this stage, further extraction will lead to membrane instability and other metals will be extracted from the photographic wastes. Some reports also indicate that the presence of salt in the receiving phase results in interfacial film breakdown which leads to membrane leakage (Oza and Frank, 1989). The formation of chloride salt in the receiving phase could explain the reduction in silver extraction when HCl was used.

Table 5.2: Percentage of silver extraction using different type of stripping agent (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, speed = 250 rpm, extraction time = 7.5 min, feed phase = real liquid photographic waste, and diluent = kerosene).

[Stripping agent]	Silver extraction (%)
1.0 M thiourea in 1.0 M HCl	70
1.0 M thiourea in 0.5 M HCl	18
1.0 M thiourea in 1.0 M H_2SO_4	98
1.0 M thiourea in 0.3 M H_2SO_4	35
0.5 M thiourea in 0.5 M H_2SO_4	42
1.0 M thiourea in 1.0 M HNO_3	17

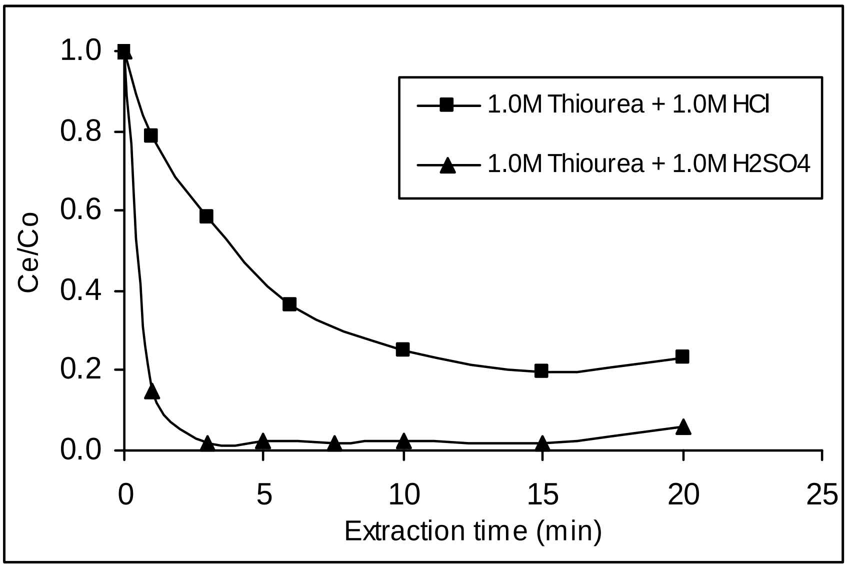


Figure 5.2: Effect of stripping agent types on the extraction of silver (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, speed = 250 rpm, feed phase = real liquid photographic waste, and diluent = kerosene).

As mentioned before, the concentration of internal stripping agent is one of the critical experimental parameters for silver extraction with liquid membranes because it moves the solutes from the membrane phase to the internal phase. Figures 5.3 and 5.4 show the effect of acid solution and thiourea concentration respectively. The results show that at fixed thiourea concentration (1.0 M), decreasing solution acidity will decrease the extraction performance. It indicates that thiourea acidity is one of the factors influencing the silver extraction in the emulsion liquid membrane system. The result shows that 1.0 M H_2SO_4 solution is acid enough for 1.0 M thiourea. Increasing the concentration to 1.5 M does not make any difference in the silver extraction performance but excess acidity may cause destruction of the emulsion in an extraction process. However, at 0.5 M H_2SO_4, the maximum extraction was about 55% and the emulsion globules were unstable after 3 minutes process. Then the extraction drastically decreases. As a result, emulsion break down and leakage occurred which reduces the extraction efficiency. This is because there are inadequate numbers of protons to form acidic thiourea as the stripping agent. As established in Chapter 4, thiourea alone cannot act as a stripping agent for silver-Cyanex 302 complexes, therefore no extraction occurred.

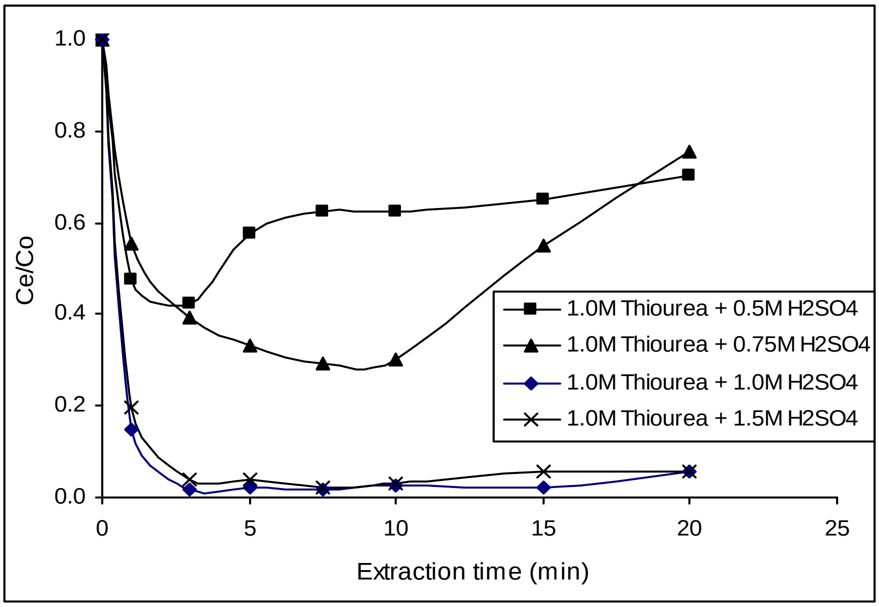


Figure 5.3: Effect of stripping agent acidity on the extraction of silver (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, speed = 250 rpm, feed phase = real liquid photographic waste, and diluent = kerosene).

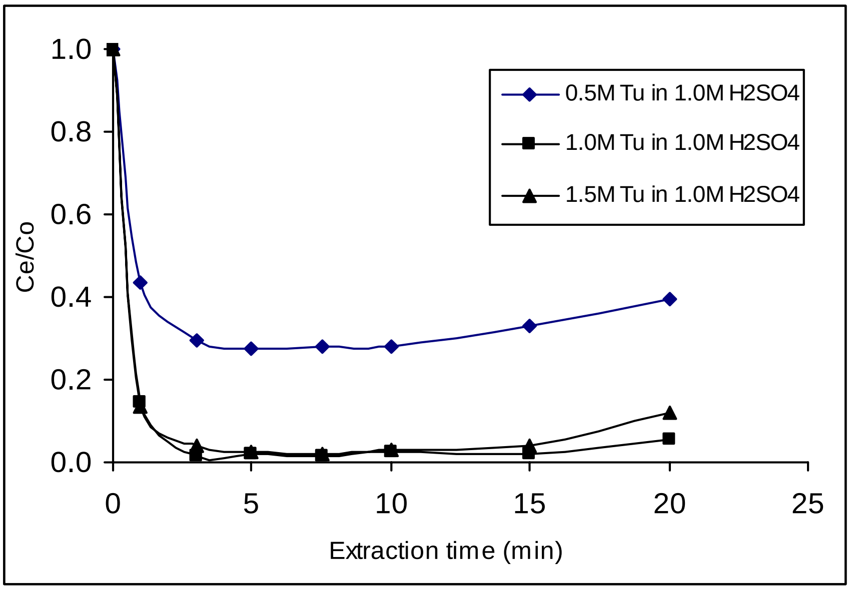


Figure 5.4: Effect of thiourea concentration on the extraction of silver (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, speed = 250 rpm, feed phase = real liquid photographic waste, and diluent = kerosene).

In addition, thiourea as a stripping reagent in the receiving phase does not affect the stability of liquid membranes because it is not surface active agent. But the reaction behavior of silver is influenced by the concentration of thiourea because thiourea forms a stable complex with silver. However, in the ELM system thiourea permeates through the liquid membrane from the internal aqueous solution to the external aqueous solution because of its solubility in the organic solution. The thiourea that permeated forms some complexes with silver in the external aqueous solution.

Furthermore, in the excess of thiourea concentration, silver is not extracted because of the formation of stable complex with thiourea in the feed solution and this complex was not transported by the carrier (Kakoi *et al*., 1993). Therefore, the degree of silver extraction increases with an increase in the concentration of thiourea, attaining a maximum value at a certain concentration but decreases again with further increase thiourea concentration.

On the other hand, increasing the thiourea concentration from 0.5 M to 1.5 M in the 1.0 M H_2SO_4 solution increased the extraction performance but at 1.5 M concentration the extraction exceeds the limiting value at which no significant increment was observed as shown in Figure 5.4. This means that there was excess of thiourea in the system but at 0.5 M thiourea the silver extraction only around 70% because of inadequate amount of acidic thiourea available to strip silver from the silver-Cyanex 302 complex. However, after 10 minutes of process time the extraction decreased due to the emulsion swelling thus providing potential for breakup over a long extraction time. In addition, the result also shows that the degree of break-up is not very dependent but the degree of recovery of silver is strongly dependent on the concentration of thiourea based on the measured extraction performance.

5.2.3 Effect of Carrier Concentration

Carrier types and its concentration plays an important role in emulsion liquid membrane formulation. It must be very selective in both external and internal aqueous phases or in metal extraction and stripping steps. Sekine and Hasegawa (1977) found that metal ion will react with extractant-containing N, O, F, P, S, and Cl. According to the Hard-Soft Acid-Base concept, silver is classified as a soft acid and soft lewis base extractant with a sulfur containing reagent paramount makes a complex with high selectivity to silver ion. So that, to what concentration must be investigate to get high extraction performance of silver in the ELM system.

The carrier concentration is closely connected with the reaction rate. When the metal ion easily reacts with the carrier to form a complex, the carrier concentration has a significant effect on the extraction rate. Shiau and Jung (1993) reported that increasing carrier (LIX 64N) concentration has great advantage in the increase of selective separation of Zn and Cd from Ni but not for selective separation of Zn and Cd because of close equilibrium values of the two with the carrier. Reis and Carvalho (1993) reported the percentage of carrier in solvent for possible extraction is between 3 – 7 %. In contrast, the extracting agent (D2EHPA) as reported by Bhavani *et al*. (1994) did not seem to affect the extraction rate for zinc. This is because of the simultaneous extraction and stripping in a coarse emulsion which keeps the loading low in the membrane phase. Hence, the actual concentration of carrier is not important as long as it is above a certain critical concentration. It means that the extraction reaction at the interface is not rate controlling.

However, in this system it was observed that Cyanex 302 concentration played a key role in ELM extraction of silver from photographic wastes. Figure 5.5 shows that by increasing the concentration of Cyanex 302 from 0.01 to 1.0 M, increased the extraction of silver and almost complete extraction was measured at 0.05 M. Further increases in the concentration results in no significant effect on extraction performance. This is because of two reasons; a maximum percentage of silver remains unstripped in the complex form (in the membrane phase) which in turn affects the final recovery by the ELM process. The other reason is with increase in carrier concentration, swelling of the emulsion was also increased, thereby diluting the stripping phase. This result coincides with the observations by Draxler and Marr (1986) and Hirato *et al*. (1990). They found that the concentration of amine extractants in the membrane phase should not be too high. High concentrations in the membrane phase have been observed to lead to high osmotic swelling and high rates of membrane breakdown. Therefore, Cyanex 302 in the liquid membrane should not be saturated with silver, but merely should act as a shuttle to carry silver ions from one side of the membrane to the other side. Since the carrier is the most expensive agent among the other liquid membrane components, its lower concentration is always preferred. Therefore, in all experiments the concentration of Cyanex 302 is maintained at 0.05 M, unless otherwise stated.

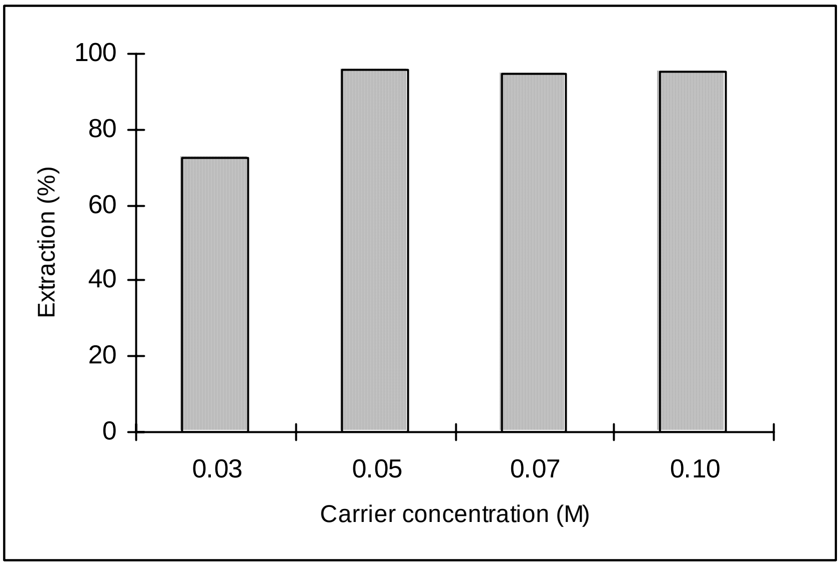


Figure 5.5: Effect of carrier concentration on silver extraction (Experimental conditions: agitation speed = 250 rpm, extraction time = 7.5 min, TR = 1:5, [Span 80] = 5% (w/v), feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M HCl, and diluent = kerosene).

Figure 5.6 shows the effect of carrier concentration in the membrane phase during the ELM extraction process. A good extraction performance was obtained at high concentration of Cyanex 302. This means that the more carrier compound existed in the liquid membrane phase, the more silver was extracted within the time. However, increasing the amount of carrier has two effects; the viscosity of the membrane phase, which limits the extraction rate and hence the carrier acts as a thinner for the membrane phase. The effect of carrier concentration on membrane viscosity was shown in Table 5.3. Therefore, increasing the carrier concentration over certain limit will decrease the stability of the emulsion and promote emulsion break-up. This finding is inline with the observation by Yan and Pal (2001).

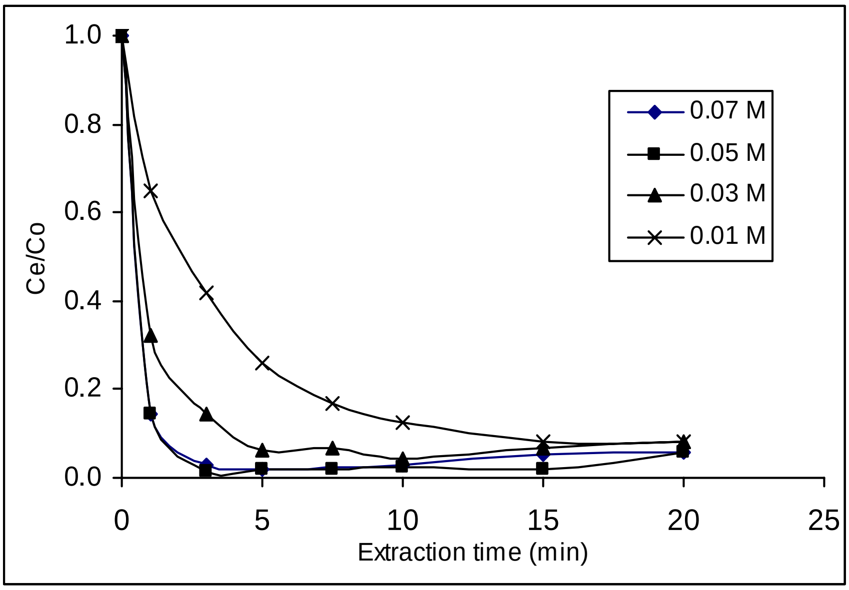


Figure 5.6: Effect of carrier concentration [Cyanex 302] on silver extraction (Experimental conditions: agitation speed = 250 rpm, TR = 1:5, [Span 80] = 5% (w/v), feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M H_2SO_4, and diluent = kerosene).

Table 5.3: Viscosity of liquid membrane (Cyanex 302 and Span 80 in kerosene).

[Cyanex 302], M	[Span 80], %(w/v)	Viscosity, cP
0.01	5	2.30
0.03	5	2.50
0.05	5	2.42
0.10	5	2.20

Figure 5.6 also shows that the increase in carrier concentration will increase the rate of solute transport (the slope of the graph) which shows the increased ability of the silver to transfer through the membrane phase via the silver-carrier complexes. It is also observed that the maximum extraction performance achieved is equal because the total amount the interior reagent is identical for all the experiments except for 0.01 M. For the 0.01 M concentration, only 90% of silver was extracted in 20 minutes extraction process while only 3 minutes was required by using 0.03 M concentration. Therefore, in this experiment longer extraction time is required for allowing the silver extraction in extraction-stripping systems. It should

be noted that further increase in the extraction time is indicative of membrane breakage and will be discussed in detail in the next section.

On the other hand, during the ELM extraction process, the pH reduces gradually in the external phase as shown in Figure 5.7. As reported, the performance of ELM operation shows better results as extraction time increased according to Figure 5.6. However, after 10 minutes process the extraction performance reduced a little bit contradict with the value of the pH system which is gradually decreased. It is due to the effect of emulsion breakage which leads to hydrogen transfer from internal phase to external phase. This finding was also observed experimentally by Zhou (1996) on strontium extraction. The experimental curve shows that when hydrogen ion concentration increases in the external phase the values of extraction distribution coefficient is decreased.

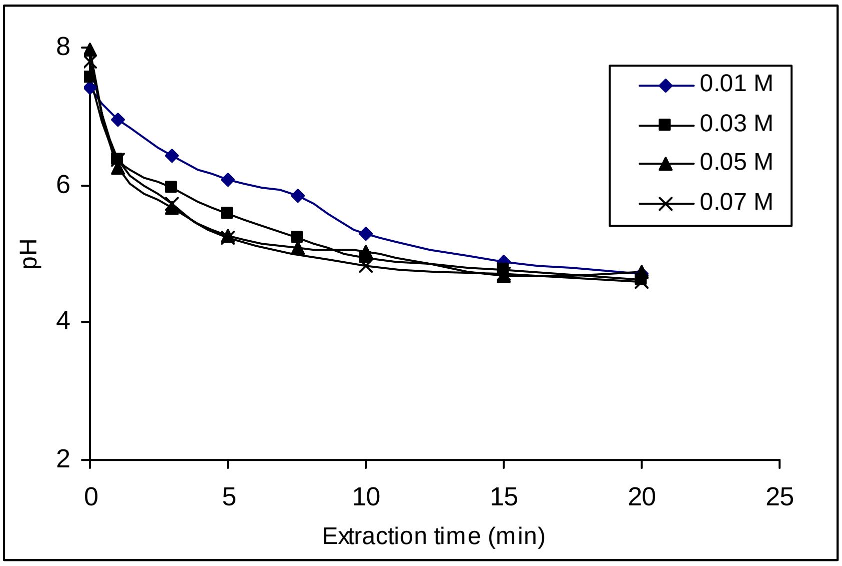


Figure 5.7: The effect of carrier concentration [Cyanex 302] on the pH of the system during the extraction process (Experimental conditions: agitation speed = 250 rpm, TR = 1:5, [Span 80] = 5% (w/v), feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M H_2SO_4, and diluent = kerosene).

The best value of the carrier concentration was found to be about 0.05 M based on the stability of the emulsion phase in the experiments. However, 0.03 M Cyanex 302 was taken to be the most appropriate concentration since the extraction percentage started to achieve its steady state after 10 minutes process time. Lower carrier concentration is always preferred because it is the most expensive agent among the other components of membrane. Although the lower carrier concentration (0.01 M) does not been give maximum extraction, a longer extraction time is not suggested due to swelling and breakage.

5.2.4 Effect of Surfactant Concentration

Since liquid membranes are thin, mobile and subject to shear, they tend to rupture during the extraction process. The stability of an ELM depends on the shear produced by agitation (Volkel *et al.*, 1980; Stroeve and Varanasi, 1984), internal droplet size (Cahn *et al.*, 1981; Frankenfeld *et al.*, 1981) and composition of the membrane (Stroeve and Varanasi, 1984; Cahn *et al.*, 1981). The composition of the liquid membrane is crucial in determining robustness and therefore many workers have studied methods of obtaining the best formulation.

Both the stability of the emulsion and the viscosity of the liquid membrane are altered by the proportion of surfactant in the organic phase (Li *et al.*, 1998). Figure 5.8 shows the effect of surfactant concentration on silver extraction from photographic wastes. As expected, as the concentration of surfactant increases in the organic liquid membrane as much the stability of the liquid membrane as its accelerative effect potential on the extraction of metal solute was grow. This fact would occur because it should increase the adsorption of the surfactant in the interface by an increase in the interface film force of surfactant molecules. Then, the emulsion droplets much more stables because of the surfactant layer adsorbed on the interfaces of the emulsion globules (Hou and Papadopoulos, 1996). If there is no surfactant used, the net interaction energy between two interfaces is attractive when they get closer, and there is no energy barrier to coalescence. As a result, the structure is thus expected to be inherently unstable, which will show an instant emulsion breakdown.

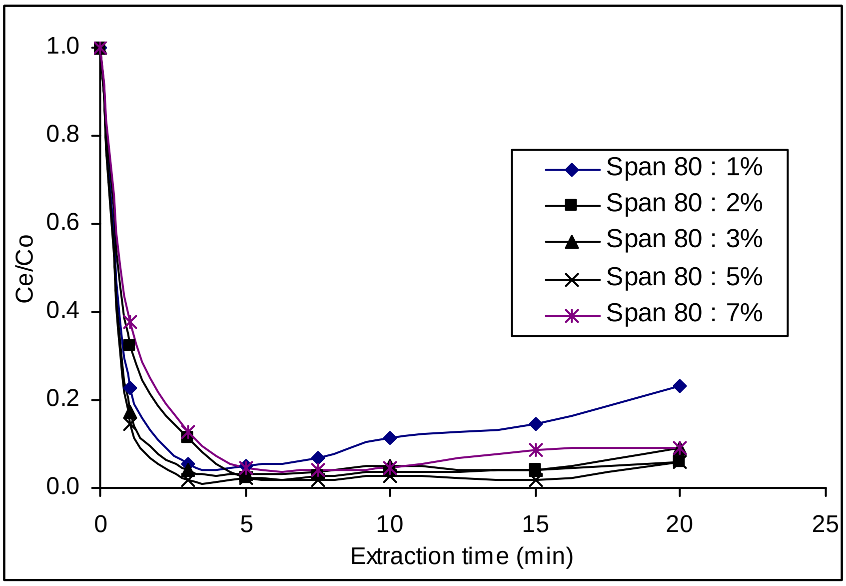


Figure 5.8: Effect of surfactant concentration [Span 80] on silver extraction (Experimental conditions: agitation speed = 250 rpm, TR = 1:5, [Cyanex 302] = 0.05 M, feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M H_2SO_4, and diluent = kerosene).

Therefore, when 1% (w/v) of Span 80 is used in this experiment, the breakage is the highest because the surfactant layer is thin. This thin layer does not have a strong influence on the interaction energy and produces no obstacle on oil film rupture. As surfactant concentration increases to 5% (w/v), the breakage rate decreases. It may be because the internal water droplet starts experiencing a net repulsive van der waals interaction with the external aqueous phase, which will produce a stable globule. However, when the surfactant continues to increase until 7% (w/v), the breakage rate starts to increase which may be caused by the swelling that cannot be observed in this experiment. Increasing surfactant concentrations from 3 to 7 % (w/v) decreases the degree of extraction (Figure 5.8).

On the other hand, emulsion stability also generally increases when the concentration of surfactant increases due to the increase in viscosity of the organic phase (Reis and Carvalho, 1993). The viscosity of the liquid membrane used in this study is shown in Table 5.4. An increase in membrane phase viscosity decreases the diffusion coefficient and mass transfer coefficient according to Equation 5.4 (Wilke-Chang diffusion coefficient correlation);

$$\mathrm{D} = 1.17 \times 10\text{-}16 \ \frac{T(\Psi M)^{0.5}}{\mu V_A^{\ 0.6}} \qquad (5.4)$$

where, the solvent association factors, ψ, for the aqueous and oil phases are 2.6 and 1.0, respectively; V_A is the solute molar volume (m^3/kg mol); μ is the viscosity of solvent (kg/m. s) and M is molecular weight of solvent (kg/kg mol) (Geankoplis, 1993; Kargari *et al.*, 2003). Therefore, if the viscosity of membrane increases the extraction rate decreases. Since there is a trade-off between membrane stability and the mass transfer rate, 3 % (w/v) of surfactant concentration seems to be suitable for the extraction.

Table 5.4: Viscosity of liquid membrane (Cyanex 302 and Span 80 in kerosene).

[Cyanex 302], M	[Span 80], %(w/v)	Viscosity, cP
0.05	1	2.02
0.05	3	2.36
0.05	5	2.42
0.05	7	2.50

In addition, a modifier can be added to the solvent with a carrier in order to modify or improve the extraction (Cote and Bauer, 1980). Substances which are preferred as modifiers are alcohols in the range of from about 10 to 13 carbon atoms and phenols such as the alkyl (8-12 carbon atom) substituted phenols, which can be added to improve extraction, phase separation and/or other important characteristics of the organic solution (Lewis, 1990).

In emulsion liquid membranes, the types and concentration of surfactant in the emulsion formulated will affect the extraction rate of metal. Both the stability of the emulsion and the viscosity of the liquid membrane were altered by the proportion of the surfactant in the organic phase. An increase in the concentration of Span 80 increased the stability of the emulsion; however the extraction of cadmium decreased (Li *et al.*, 1998). A similar effect was observed by Reis and Carvalho (1993) in the recovery of zinc. It also increased the viscosity and resulted in the reduction of diffusivity of the metal complex in the organic phase. Thus, there exists a trade-off between membrane stability and the mass transfer rate. Surfactant concentrations of 1 to 2 % are sufficient for obtaining a stable emulsion, even if the viscosity of the diluent is as low as 1 – 2 cP (Draxler and Marr, 1986).

As a result, ECA 4360 is preferred to SPAN 80, mostly due to lower osmosis or it transport much less water. The water content in the emulsion can increase from 10-20% to 30-50% wt (Hu and Wiencek, 1998). The swelling reduces the stripping reagent concentration in the internal phase which in turn lowers its stripping efficiency. Meanwhile, the leakage of the internal-phase content into the feed stream because of membrane rupture not only releases extracted metals back into feed stream but further contaminates the feed stream with stripping reagents. Swelling and leakage can be minimized by making a more stable emulsion with a higher concentration of surfactant, but this makes the downstream de-emulsification and product recovery steps more difficult. Lower shear rates would also minimize leakage, but mass transfer resistance could then become very significant.

5.2.5 Effect of Agitation Speed

While the components of the emulsion are of vital importance to the ELM process, the process conditions like reactor hydrodynamics also plays a significant role in the system and must be chosen carefully. The speed of agitation plays a major role in the rate transfer of solute through the liquid membrane. Increasing a level of agitation would increase the interfacial area and mass transfer coefficient, but at to certain level of agitation the emulsion droplets are likely to break and therefore reducing overall enrichment and extraction in molybdenum extraction (Prashant and Kumar, 2002). It is also reported that by increasing the agitation speed from 100 to 200 rpm the rate of extraction increased but 200 to 400 rpm resulted in reduction of extraction. At high agitation rate hydrodynamic shear and swelling work together causing lower extraction. It also occurred in extraction of zinc (Bhavani, 1994), where increasing the speed above 350 rpm may further increase extraction rate, but the higher shear would also increase the leakage rate from the internal phase making the extraction inefficient.

The effect of agitation speed in the silver extraction process from photographic wastes by using different internal reagent solutions was shown in Figures 5.9 and 5.10. It was observed that by increasing the agitation speed from 200 to 250 rpm caused the rate of extraction to increase but when using thiourea in the HCl solution the stability of emulsion collapsed because of hydrodynamic effect after minutes 7 and 1 at 200 rpm and 250 rpm respectively. This was due to an increase in the volumetric mass transfer coefficient in the aqueous feed phase (between the emulsion globules and the aqueous solution), but a further increase in speed of agitation from 250 to 350 rpm resulted in a reduction in the extent of extraction as illustrated in Figure 5.10. The effect of hydrodynamic instability due to swelling is a very complex phenomenon. At a microscopic level, some particles are being broken because of shear after reaching a larger size. At the same time swelling is also increasing. There exists a trade-off between these two effects. The swollen particles can breakdown on their own or breaking is induced by shear. At 300 rpm, despite high swelling the breakage indicated less extraction and enrichment. It should be noted that the effect of extraction is less at 300 rpm compared to that at 200 rpm during 10 minutes of extraction times. Therefore, the speed of agitation plays an important role in a mechanically agitated contactor.

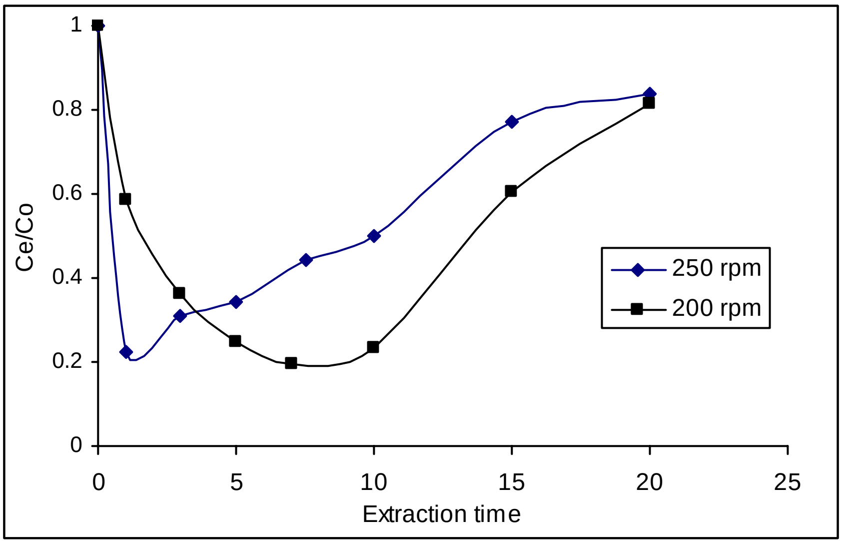


Figure 5.9: Effect of agitation speed on the extraction of silver (Experimental conditions: TR = 1:5, [Span 80] = 5 %(w/v), [Cyanex 302] = 0.05 M; feed phase = real photographic waste, stripping phase = 1.0 M thiourea in 1.0 M HCl, and diluent = kerosene).

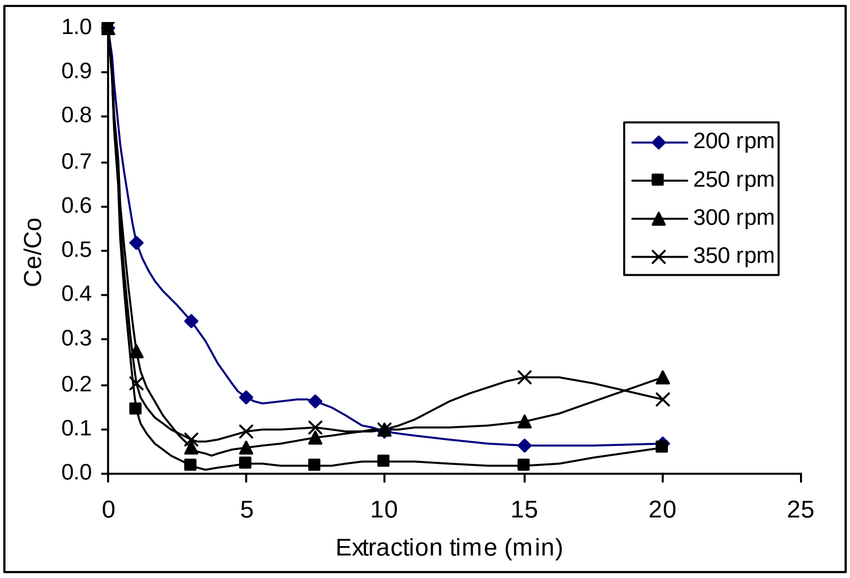


Figure 5.10: Effect of agitation speed on the extraction of silver (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, feed phase = real liquid photographic waste, stripping phase = 1.0 M thiourea in 1.0 M H_2SO_4, and diluent = kerosene).

Figures 5.9 and 5.10 also show the rate of silver extraction increased as the agitation speed increased. It was presented by the slope of the graph. It is indicated that the rate of extraction reaction depends more on how fast the solute transfer to a reaction interface. At high speed, the solute transfers very fast but some how these solutes cannot be extracted immediately because of its procession in the external-membrane interface.

5.2.6 Effect of Treat Ratio (TR)

The treat ratio is defined as the ratio of emulsion phase volume (V_m) to the aqueous feed phase volume (V_{III}). It plays an important role in determining the effectiveness of the ELM. The treat ratio was varied by changing the amount of feed phase and keeping the volume of the emulsion constant. Figure 5.11 exhibits the effect of treat ratio on the extraction of silver and swelling of emulsion. The treat ratio was varied from 0.143 (V_m:V_{III}=1:7) to 0.33 (V_m:V_{III} =1:3). As shown in Figure 5.11, there was a steady increase in the extraction of silver with increasing values of V_m:V_{III}, while from observation the swelling of emulsion had no profound effect. With an increase in the treat ratio, the volume of emulsion as a whole increased. Therefore, the surface area for mass transfer increased owing to the formation of a larger number of emulsion globules. As a result, a higher degree of extraction was obtained. A lower treat ratio means that less emulsion is used to extract silver, which is desired from the process point of view to have maximum enrichment of silver with respect to the feed phase. The result also shows that at treat ratio 1:7 silver extraction was about 56% at 3 minutes process time; however the concentration of silver in the feed phase increased yet again. It is because the droplets did not contain enough internal reagents to react with the solute transported through the liquid membrane. As a result, extracted silver (the carrier-silver complex) accumulated in the membrane phase and no carrier diffused back to react with silver in the external phase. Meanwhile, water transportation by the surfactant still carries on. Therefore, the rate of swelling increased as recorded in Table 5.5. Consequently, the concentration of silver in the feed phase increased.

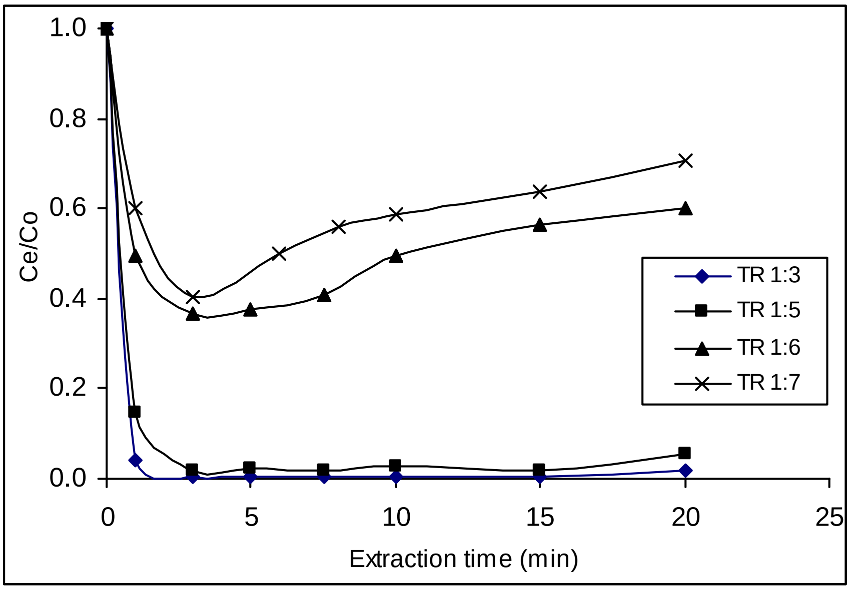


Figure 5.11: Effect of treat ratios on the silver extraction (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 5 %(w/v), [Cyanex 302] = 0.05 M, feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M H_2SO_4, and diluent = kerosene).

Furthermore, the extraction performance increases with increasing the treat ratio because the total interfacial area between the external phase and emulsion drops, and the capacity of internal phase for trapping silver increases simultaneously. This has been attributed to shorter diffusion lengths as the packing of the droplets becomes tighter. However, further increase in the treat ratio is not feasible because of the increase in water transport to the interior phase, which strongly influences on emulsion swelling. Table 5.5 shows the effect of apparent swelling with treat ratio. Similar effect was reported by Li *et al*. (1996) and Reis and Carvalho (1993) in mercury and zinc separation respectively.

Table 5.5: Effect of treat ratio on emulsion apparent swelling.

Time	Apparent swelling (%)		
	TR 1:3	TR 1:5	TR 1:7
1	8	4	2
3	8	4	3
5	10	10	5
7.5	10	10	10
10	10	10	12
15	8	6	12
20	0	10	12

Li *et al*. (1996) reported that in mercury separation, varying the emulsion to feed volume ratio from 1.75:10 to 2.5:10, the experimental result showed that the concentration of mercury in feed decreased after 10 minutes, meaning that the extraction efficiency was increased. It is indicated that increasing value of treat ratio suchlike increasing emulsion volume over the feed phase that will increase the extraction performance as a result of many reason as discussed. The similar results was found in this experiment where by increasing the treat ratio, the extraction performance was increased but the high apparent welling was observed during the initial period of process,

Another point to consider is the pH values in the external phase. During the extraction process it was found that the pH of the system decreased with extraction time. As discussed in Chapter 4, an acidic carrier will liberate hydrogen ion during the reaction of carrier and metal ions. It means that the more hydrogen ion is released the more metals ion were extracted. This phenomenon was illustrated by the pH value of external phase. The pH value of the system with treat ratio 1:3 and 1:7 are 3.97 and 5.63 respectively at 20 minutes extraction. It is indicated that the performance of extraction can also be measured based on liberation of proton during the extraction process.

Figures 5.11 and 5.12 also show that the rate of extraction was very fast in the first 5 minutes time. It was presented by the slope of silver extraction and the pH changes during the extraction process. By increasing the treat ratio, the slope of the graph increase, indicating that the reaction performance at membrane and feed phases increased due to the more interfacial area and the shorter diffusion distance as discussed before. Therefore, a reasonable treat ratio was selected to be economically feasible. In this experiment, a 1:5 treat ratio was selected as the optimum value because of its highest percentage of extraction and percentage of swelling are in moderate value compared to 1: 3. From the economical point of view, the highest treat ratio will reduce the employment of expensive carrier and increase the amount of waste treated.

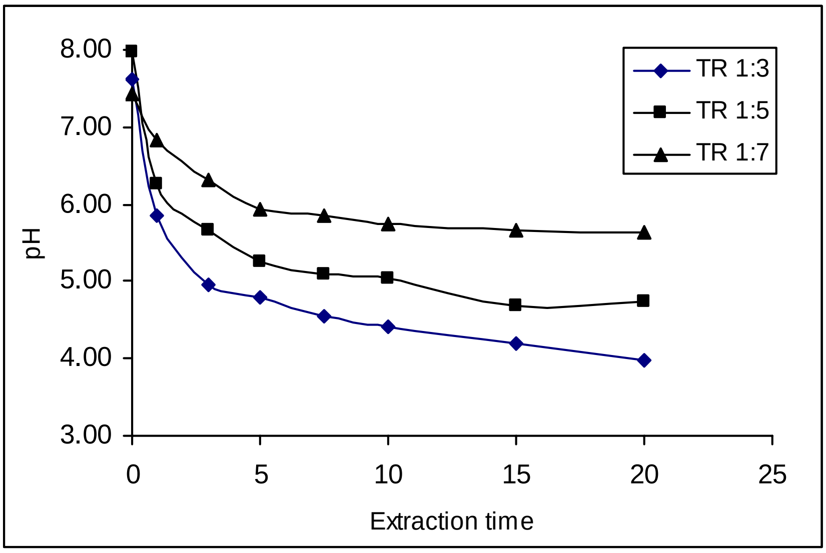


Figure 5.12: The effect of varies treat ratio on the pH of the system (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M H_2SO_4, and diluent = kerosene).

5.2.7 Effect of Diluents

The viscosity and the density of the diluents are also the main parameters which determine the thickness of the membrane and permeability of the membrane for the solute. Change of organic diluents in the emulsion preparation produces changes in emulsion stability, percentage of extraction, enrichment factor and swelling.

The diluents employed in the solvent extraction systems generally are considered to be chemically inert. However, an extensive study by Ritcey and Lucas (1974) has shown that diluents can play a substantial role in determining the success of the solvent extraction operation. It is accepted that the role of the diluents is complex and that the extraction behaviour cannot be attributed to any particular physical or chemical property of the diluents. The selection of diluents must therefore be based on the chemical components of the diluents, and its physical characteristics such as dielectric constant, its polar nature and the solubility parameter. The rate of phase separation may, in the final consideration, be the determining factor in the selection of the diluent for a particular system.

It is recognized that the organic diluents influence the performance of many liquid membrane system (Gu *et al.*, 1992; Saji *et al.*, 1998; Tutkun *et al.*, 1999). In the context of solvent extraction, it should be noted that aromatic content refers to all molecules containing a benzene ring. In addition better extraction was obtained with aliphatic diluents than with aromatic diluents (Bailey and Mahi, 1987; Murry and Bouboulis, 1973; Ritcey and Lucas, 1974) and they also conclude that the chemical composition affected the performance of the diluents. The amount of aromatic constituent in the diluents generally reduced the percentage of metal extracted. Ritcey and Lucas (1974) suggested that the diluents becomes less inert towards the metal ion as the aromatic content is increased and the diluents may be incorporated in some way into the extractable species.

In addition, the extraction of the metal decreases with an increase in both the polar nature and the dielectric constant of the diluents employed (Ritcey and Lucas, 1974). Interaction of the diluents with the extractant will then result in lower metal extraction values. Thus the formation of an extractant-diluents species in the organic phase produces a lower concentration of the ‘free extractant’, with a consequent decrease in the overall extraction values.

The experimental results obtained agree with the work of other researchers. Figure 5.13 shows that the extraction performance of silver decreased in the following order:

kerosene > n-dodecane > toluene.

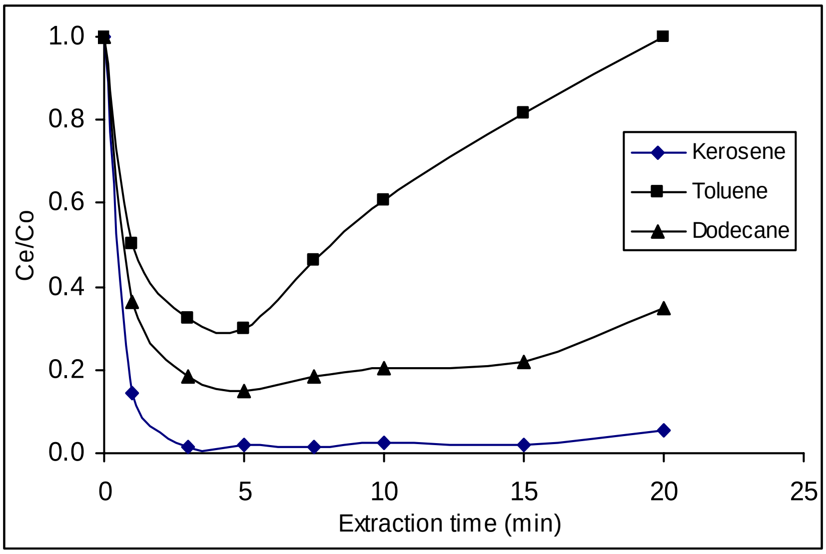


Figure 5.13: Effect of diluents on the silver extraction (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, feed phase = real photographic wastes, and stripping phase = 1 M thiourea in 1 M H_2SO_4).

It was indicated that aliphatic diluents are generally preferred because of the lower solubility in water and better emulsion stability. The performance of silver extraction was almost stable during the 20 minutes process when using kerosene as diluents. The same trend was expected for emulsion stability due to less transport of water. This result contradicts with toluene and n-dodecane where extraction started to decrease after 5 minutes. This was indeed the case and this process has membrane stability in the same order. These observations are in line with those by Kinugasa *et al.* (1989) which examined the effect of several organic solvents on the membrane stability. Further, compared to the paraffinic diluent, the aromatic diluent tends to readily break down under shearing conditions. Therefore extraction was found to be decreased in the following order: kerosene > n-dodecane > toluene. This clearly indicates that kerosene has a higher viscosity organic phase which produces higher extraction and lower percentage of swelling than the others. The higher number of carbon atoms in kerosene and n-dodecane means a higher hydrophobicity which results in less transport of water across the membrane than toluene. Kurkarni *et al.* (2003) studied the effect of viscosity on metal extraction and found that the viscosity or thickness of the membrane determines the rate of transport with added heavy paraffin into the diluents. It was found that increase in viscosity of membrane increased the stability and extraction time of the emulsion and hence decreased the percentage of extraction.

Therefore, it is possible for diluents to be selected for a particular process based on the chemical composition of the diluents and the physical characteristics such as the dielectric constant, dipole moment, the extent of hydrogen bonding and the modified solubility parameters. However, from the obvious environment point of view, paraffinic solvents are most preferred to aromatic diluents. It appears that kerosene-type diluents are the most suitable solvents for industrial operations due to relatively high flash point and high metal extraction value.

Furthermore, a diluent is normally employed to decrease the viscosity of the extractant solution, to provide a suitable concentration for the extractant, to decrease the emulsion-forming tendencies of the extractant, and/or to improve the dispersion and coalescence properties of the solvent. A modifier can also be used to overcome the formation of a third phase, which is essentially a solubility problem of the diluent. Both the diluent and the modifier affect the extractant and extracted species through molecular interactions, such that the extractability or extraction equilibrium formulation changes dramatically (Nishihama *et al.*, 2001).

5.2.8 Effect of Homogenizer Speed in Emulsification

The purpose of this experiments was to determine how different emulsification processes especially homogenizer speed affect the extraction efficiency. Three speed of homogenizer 8000, 9500 and 13500 rpm were tested in 5 minutes emulsification process. Figure 5.14 shows the extraction performance among three speeds. Clearly, 13500 rpm was found to be better than 9500 rpm and

8000 rpm during 20 minutes extraction. It is because the size of the emulsion droplet was based on homogenizer speed as discussed in Chapter 4. The smaller the emulsion droplet, the more number of emulsions is produced in certain volume and the surface area definitely increased. Therefore, the extraction performance also increased.

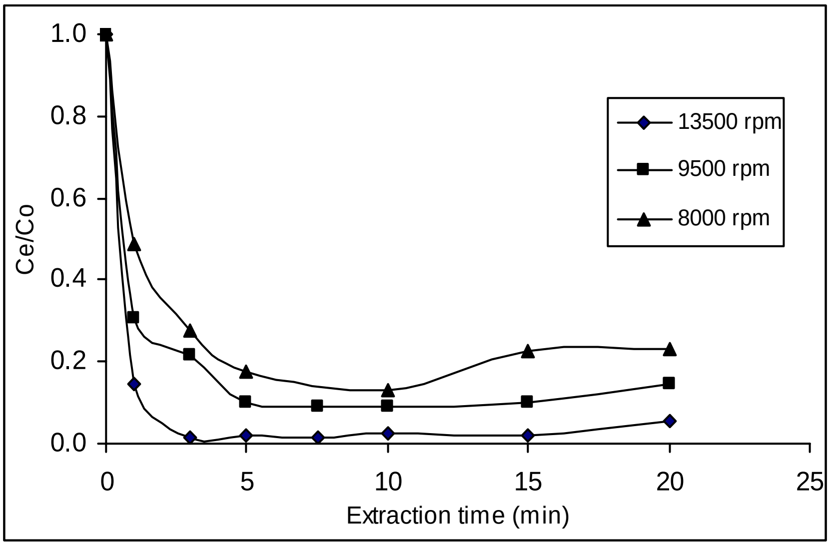


Figure 5.14: Effect of homogenizer speed on the silver extraction (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 5 % (w/v), [Cyanex 302] = 0.05 M, feed phase = real photographic waste, and stripping phase = 1 M thiourea in 1 M H_2SO_4).

5.2.9 Metal Selectivity

Selectivity is a key consideration in any separation process. As photographic wastes usually contain many anions and cations, the ability of the membrane to transport only the target metal ion becomes an important factor. Selectivity in carrier-mediated ELM processes is governed primarily by the carrier used in the liquid membrane formulation.

Figure 5.15 and Table 5.6 show that the ELM process using Cyanex 302 is very selective toward silver which is almost completely extracted from the other metals in 3 minutes. This is in agreement with the result in Section 4.2 when Cyanex 302 is used as an extractant in a solvent extraction process. However at longer extraction times it was found that the percentage of other metals increased especially after 10 to 20 minutes. As the extraction time increased the reaction of the carrier with the other metals such as sodium, potassium and iron still continued at the membrane/feed phase interfaces, while silver was completely extracted earlier in the process. As reported in Section 4.1 the percentage of iron extraction increased when the pH in the system decreased. This similar effect occurred during the ELM operation. As recorded the pH in the feed phase decreased during the extraction process and proved by Equation 5.1 in which one hydrogen ion was released for one mole silver-carrier complex formed.

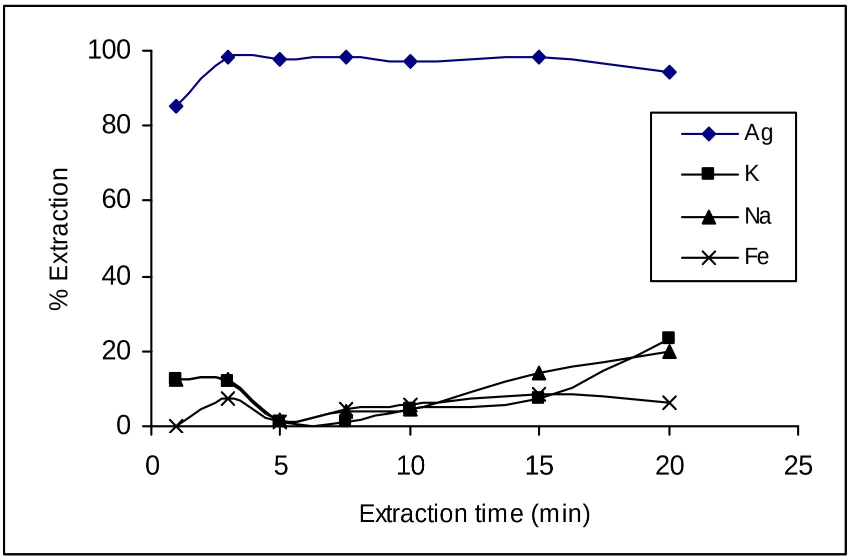


Figure 5.15: Metal selectivity in ELM extraction process (Experimental conditions: TR = 1:5, [Span 80] = 5% (w/v), [Cyanex 302] = 0.05 M, speed = 250 rpm, feed phase = real liquid photographic waste, stripping agent = 1.0 M thiourea in 1.0 M H_2SO_4, and diluent = kerosene).

Table 5.6: Selectivity of silver from photographic waste in 20 minutes ELM extraction (Initial [Ag] = 2050 ppm, [Fe] = 2000 ppm, [K] = 6890 ppm, and [Na] = 3230 ppm).

Time (min)	$S_{Ag/Fe}$	$S_{Ag/K}$	$S_{Ag/Na}$	$S_{Ag/(Fe,K,Na)}$
0	0.00	0.00	0.00	0.00
1	4363.51	40.67	40.50	20.20
3	751.56	449.13	411.02	166.94
5	5068.86	3569.56	2821.31	1202.10
7.5	1188.81	4690.36	1345.23	556.25
10	606.95	809.59	800.23	241.99
15	548.22	626.65	304.13	149.08
20	244.75	55.22	66.22	26.81

Figure 5.15 also shows that at 15 to 20 minutes extraction time, the percentage of silver extraction slightly decreased; this means that the silver appear again in the feed phase after having been absent for a few minutes. This is due to the instability of the emulsion over longer extraction times. Increasing the extraction time makes the emulsion to swell and break down after a certain time. The swelling will decrease the efficiency of metal recovery and when breakage occurs, the stripped metal leaks from the receiving phase to the feed phase and the amount of silver in the feed phase will increase. If the extraction process is continued to longer extraction times the emulsion liquid membrane performance will collapse.

Moreover, the type and concentration of anionic species present in the aqueous phase affect the extraction behavior of metals. It can generally be expected that if the stability of a metal complex in the aqueous phase is greater than that of the metal-extractant complex, then extraction would not be possible as reported in Chapter 4.

5.3 Emulsion Liquid Membrane Extraction Using Different Types of Carrier

As reported in Chapter 4, another potential type of carrier is tetramethylthiuram disulfide (TMTDS). Tetramethylthiuram disulfide (TMTDS) is used as the mobile carrier because it is an efficient extractant reagent for silver in thiosulfate media based on the screening test using solvent extraction technique. TMTDS, as a chelating extractant is incorporated in the membrane phase to increase the mass transfer rate due to the large interfacial area. Span 80, a nonionic surfactant is added to form a stabilized liquid membrane.

In W/O/W systems, the nature and the properties of the organic phase are very important because it acts as a semi permeable membrane separating two aqueous phases. Hence, non-polar or medium polar diluents are recommended for the formulation of W/O/W emulsions. Toluene is used as the diluent for TMTDS because it is a non-polar aromatic hydrocarbon which has a density of 0.86 g/cm^3 and a viscosity of 0.68 centistokes at 30 ˚C. It is preferred in the formation of organic phase due to its hydrophobicity which results in less transport of water across the membrane. Table 5.7 shows the experimental condition for this study.

Table 5.7: Experimental conditions used for the preparation of ELM.

Parameters	Conditions
[TMTDS]	0.01-0.07 M in toluene
[Span 80]	3-7 % (w/v)
Treat Ratio	1:3, 1:5, 1:7
Stirring speed	200-350 rpm
Organic phase	V_{org} = 5 mL
Internal aqueous phase	V_i = 5 mL
Stripping agent	1 M thiourea in 0.01-0.1 M HCl

The effect of agitation speed was studied in the range of 200-350 rpm. Theoretically, increasing the agitation speed will increase the extraction performance due to reduction of the emulsion globule size thereby providing a high interfacial contact area between the external and membrane phases and increase in the external phase mass transfer coefficient. However, increasing the agitation speed above a critical level not only does not increase the extraction performance considerably, but rather break down the emulsion globule and thereby reducing overall extraction efficiency.

From Figure 5.16, it was observed that there were two zones of speed range; (1) 200-250 rpm and (2) 300-350 rpm that manifested the same trend in which the extraction percentage decreased with an increase in emulsion breakage percentage. In zone (1), the extraction performance does not increase with the agitation speed because the emulsion break-up dominated in the extraction process and its effect overtook the influence of agitation speed in the ELM process. The same phenomenon occurred in zone two. It seems that there is a transition zone between 250 and 300 rpm where the emulsion globules may undergo some size adjustment caused by hydrodynamic shear and also the shear induced by the magnetic stirrer in the extractor. At 300 rpm, the extraction performance was at its optimum condition where there was no emulsion break-up observed at the particular speed. From the overall process point of view, however increasing the speed of agitation from 200-300 rpm indeed increased the extraction performance and reached its critical value at 350 rpm where the degree of extraction started to decrease in zone (2).

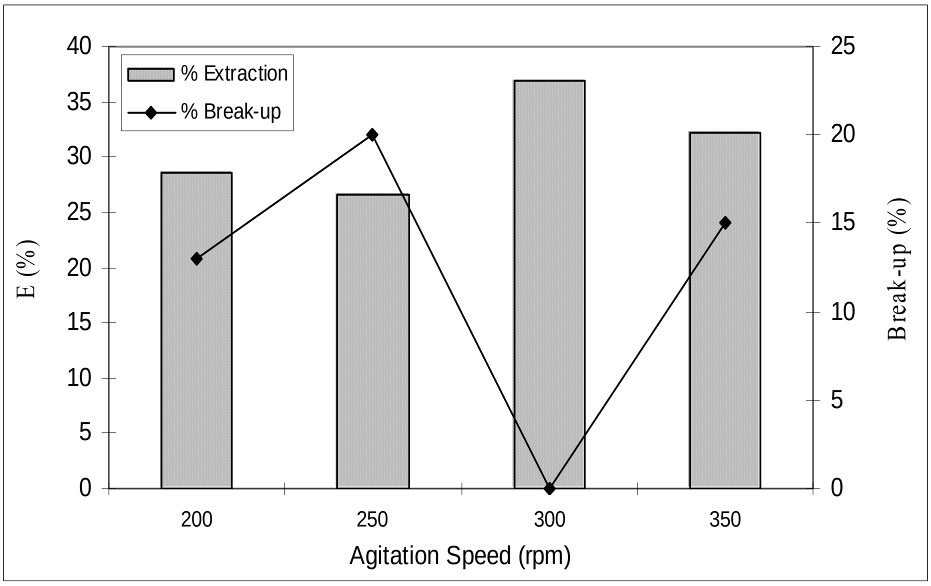


Figure 5.16: Effect of agitation speed on the extraction and break-up of emulsion (Experimental conditions: [TMTDS] = 0.03M in toluene, [thiourea] = 1 M in 0.1 M HCl, extraction time = 6 min, [Span 80] = 5 % w/v, and treat ratio = 1:5).

On the other hand, both the stability of the emulsion and the viscosity of the liquid membrane were altered by the proportion of surfactant in the organic phase. The effect of surfactant concentration on silver extraction is exhibited in Figure 5.17. The data on the viscosity of the organic phases with varying surfactant concentration using 0.05 M TMTDS extractant and toluene as diluent is presented in Table 5.8.

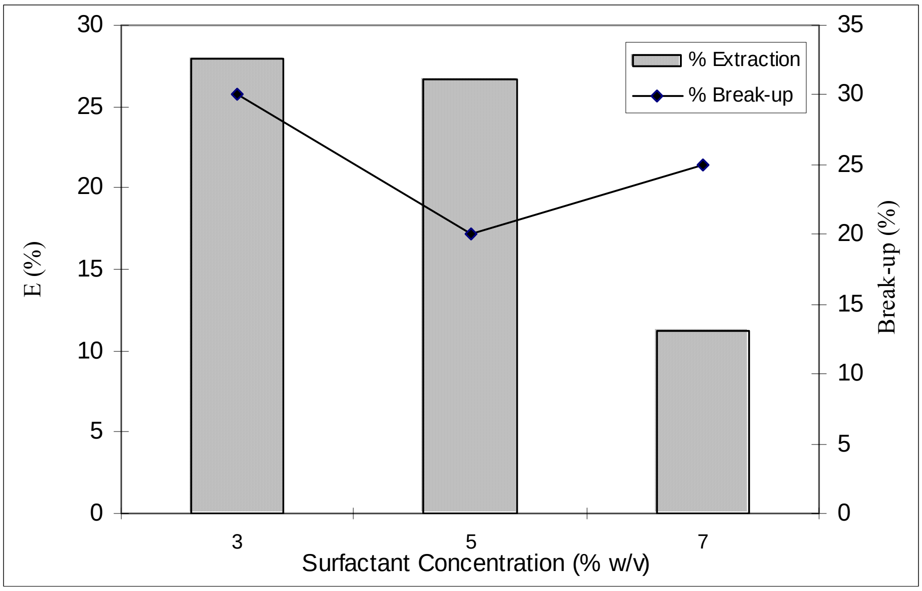


Figure 5.17: Effect of surfactant concentration on the extraction of silver (Experimental conditions: [TMTDS] = 0.03M in toluene, [thiourea] = 1 M in 0.1 M HCl, stirring speed = 250 rpm, treat ratio = 1:5, and extraction time = 6 min).

Table 5.8: Dependence of viscosity of the organic phase used for emulsion preparation on surfactant concentration.

[Span 80], % (w/v)	Viscosity (μ) at 30 ˚C and 100 rpm (cP)
3	1.11
5	1.35
7	1.59

Since there is no swelling observed in this experiment, the attention will be given to the membrane viscosity and emulsion break-up. Emulsion stability generally increased with increasing concentration of surfactant. This is attributed to the increase in viscosity of the organic phase. Based on the literature, a surfactant layer adsorbed on the interfaces of the globules represents the amount of surfactant present. If there is no surfactant used, the net interaction energy between two interfaces is attractive when they get closer and there is no energy barrier to coalescence.

Therefore, when 3% w/v of Span 80 is used in this experiment, the emulsion breakage is the highest because the surfactant layer is thin. These thin layers do not have a strong influence on the interaction energy and produces no obstacle on oil film rupture. As surfactant increased to 5% w/v, the breakage percentage decreased. It maybe because the internal water droplet starts experiencing a net repulsive van der waals interaction with the external aqueous phase, which will produce a stable globule. However, when the surfactant continues to increase until 7%, the breakage rate starts to increase which maybe caused by the swelling.

As shown in Figure 5.17, increasing surfactant concentration from 3 to 7 % (w/v) decreased the degree of extraction. As a result, the mass transfer was affected. Based on the Wilke-Chang diffusion coefficient as discussed in Section 5.2.4, an increase in membrane phase viscosity will decrease the diffusion coefficient and mass transfer coefficient. Therefore, when the viscosity of membrane increased from 3 to 7 % w/v, the extraction percentage decreased.

Since thiourea has both basic and acidic groups, dependence of the extraction efficiency on the pH in the internal phase is important. Thiourea (1.0 M) solutions of different acidity have been prepared by adding HCl with different concentration before mixing with the organic phase to form emulsion. Figure B1 in Appendix B shows the effect of HCl concentration on silver extraction. From the results, it can be concluded that the extraction efficiency increased with an increase in the acidity of thiourea solution from 0.01 to 0.1 M HCl. Therefore, 0.1 M HCl will be selected as the favorable acidity for thiourea solution in this study.

Figure 5.18 shows the extraction performance of tetramethylthiuram disulfide (TMTDS) as a mobile carrier of silver from photographic wastes. In the initial stage, the extraction rate increased rapidly because the large interfacial area provided by the emulsion globules enhanced the mass transfer of the silver ions. Therefore, the diffusion of solute-carrier complex across the membrane also increased. After minute 2, there was a slight decrease in the extraction percentage that maybe caused by the emulsion break-up, but the effect is marginal. By using the optimum conditions, the silver extraction can reach higher extraction rate until 89.7 % at 15 minutes operation. After that, there was no further increase in the extraction percentage because the local reaction at the external interface between the external and the membrane phases is in equilibrium. From the observation, the overall break-up rate is less than 10%. As a conclusion, TMTDS is an effective extractant that can be used in the ELM process in order to extract silver ions from photographic waste. Further studies on the parameters effect is discussed in Section 5.2.

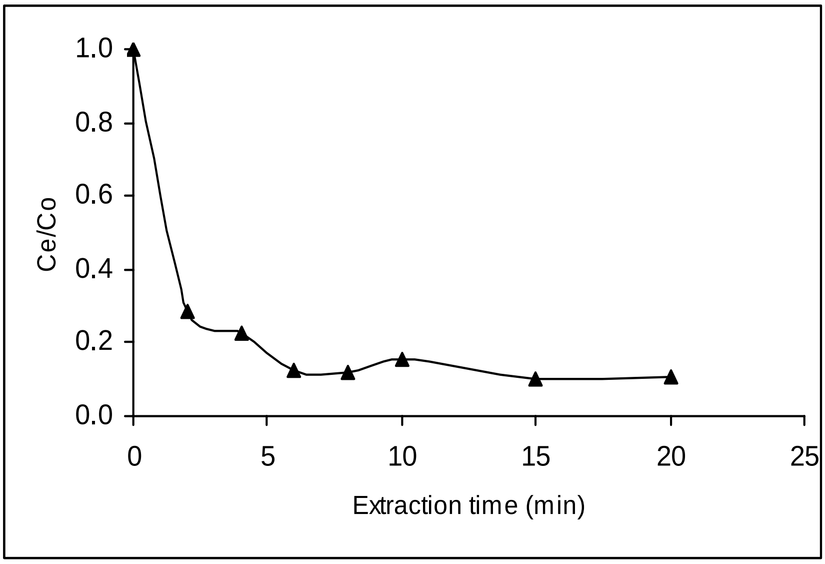


Figure 5.18: Extraction of silver from photographic wastes (Experimental conditions: [TMTDS] = 0.05 M in toluene, [thiourea] = 1M in 0.1 M HCl, agitation speed = 300 rpm, [Span 80] = 5% w/v, treat ratio = 1:5).

5.4 Membrane Breakage and Swelling

5.4.1 Introduction

The integrity of the membrane or more specifically the lack of membrane breakage and swelling is vitally important to the efficiency of the ELM-mediated separation. Membrane breakage can occur through hydrodynamic shear (Stroeve and Varanasi, 1984), emulsion composition (Stroeve and Varanasi, 1984; Takahashi *et al.*, 1981) and emulsion preparation (Hanna and Larson, 1985). In the formation of ELM process, water transported into the inner aqueous phase results in swelling of emulsion. Significant swelling will dilute the concentration of the substances concentrated in the inner aqueous phase, lower the selectivity of separation, changes the viscosity of the system and the dispersity of emulsion, and affects separation of the W/O emulsion from the external phase and demulsification process. It was reported by Matsumoto *et al*., (1980) that the entering of water in the inner aqueous phase is due to an osmotic gradient. However some researchers have proposed several different mechanisms to explain the swelling of ELM globules. The proposed mechanisms are:

i) Molecular diffusion (Colinart *et al*., 1984) of water from external aqueous phase to internal aqueous droplets;
ii) Micelle assisted transport of water from the external aqueous phase to internal water droplets (Garti *et al*., 1985) accordingly; water transport is facilitated through the membrane (oil) phase by reverse micelles of surfactant present in the membrane phase;
iii) Transfer of water from the external aqueous phase to internal water droplets via hydration of surfactant molecules (Colinart *et al*., 1984) ; and
iv) Entrainment and emulsification of the external aqueous phase in the emulsion globules due to excess surfactant present in the primary emulsification step (Kinugasa *et al*., 1989; Ding and Xie, 1991; Skelland, 1999; Itoh *et al*., 1990).

The first three mechanisms predominate in most situations although swelling can also take place due to the fourth mechanism. It is important to realize that for water transport (swelling) to take place by the first three mechanisms, the presence of the osmotic pressure gradient between the external and internal aqueous phases is necessary. In ELM extraction processes, the osmotic pressure gradient between the external and internal aqueous phases is generally present as the concentration of the solute is different in the two phases.

Water transport through the ELM can be measured in a variety of ways, depending on the particular experiment being run. For batch experiments that examined the effects of process parameters, swelling was determined by mass balances at the end of the experiment. For continuous experiments, swell was evaluated by using a non-reactive tracer and for swelling experiments when no carrier was present in the membrane phase, the degree of swelling was calculated using densitometry (Thien and Hatton, 1988). Matsumoto *et al.* (1980) was the first to study the permeation of water in W/O/W membranes using optical microscopy. The permeation of water was characterized in terms of the permeation coefficient at the beginning of swelling, P_0. The permeation coefficient at the beginning of shrinkage, P_0 was determined from the droplet size data of ELM globules. A coulter–counter technique was used to measure the diameter of ELM globules as a function of time. With the increase in the surfactant concentration of the membrane phase, Garti *et al.* (1985) found a significant increase in the permeation coefficient. This contradicts the observation of Matsumoto *et al.* (1980) that P_0 decreases with the increase in surfactant concentration.

Furthermore, emulsion swelling is a phenomenon that occurs during the dispersion operation, leading to changes in the volume of emulsion and internal phase. Obviously, both emulsion swelling and membrane breakage occur simultaneously during the operation, and both cause the change in the volume of the internal phase. Therefore, the calculation of emulsion swelling ratio is simply based on the final volume of emulsion or the internal phase after operation in most of the papers published (Wan and Zhang, 2002). This implies the combined effect of both emulsion swelling and membrane breakage, and thus Wan & Zhang (2002) call it 'apparent swelling' which is discussed in this section while the emulsion swelling caused by the osmosis and entrainment is called 'actual swelling' that is measured by internal phase droplet size variation method (Li and Shi, 1993; Garti *et al.*, 1985; Collinart *et al.*, 1984) was not considered. Therefore, in this study, the volume difference in the internal phase was measured as an indicator of 'apparent swelling' in the process based on Wan and Zhang (2002) theory. Thus, the apparent swelling ratio $(\eta_{s,ap})$ in this study is expressed by the following equation:

$$\eta_{s,ap} = \frac{V_i - V_i^o}{V_i^o} x100\% \tag{5.5}$$

where, V_i is the volume of the internal phase after operation and V_i^0 is the initial volume of the internal phase.

5.4.2 Effect of Agitation Speed

The power delivered to the extractor from agitation is an important parameter in ELM systems. The size of the globules strongly depends on the mode and intensity of the mixing (Matulevicius and Li, 1975). From experimental results (Li and Shrier, 1972), the emulsion globules are typically in the range of 0.05 to 0.2 cm in diameter. Thus, a very large number of emulsion globules can be formed easily to produce a very large mass transfer area adjacent to the external feed phase. On the other hand, each globule contains many 10^{-2} to 10^{-4} cm internal droplets. Therefore, a rapid mass transfer in the emulsion liquid membrane process can occur from the external feed phase to the internal phase. Because high speed or stirring will lead to the easy breakdown of the emulsion globules, the suitable speed should be found by trial. Thus, a series of experiments were conducted where the agitation speed was varied from 200 to 400 rpm (Figure 5.19) within 10 minutes contact time to examine the extraction behavior and break-up of the emulsion due to different agitation speeds. As stated before the increasing speed will increase the mass transfer rate means that the extraction increased but at certain limit of speed the emulsion tends to break and the metal will diffuse back to the feed phase. As a result the extraction performance become lower and the break-up will increase. However, in these range of speeds (200 to 250 rpm), the percentage of extraction increased because mass transfer rate is faster and defeats the break-up rate. Actually the formation of dispersions is governed by two competing process such as drop break-up and drop coalescence. Initially, the bulk of the liquid in the dispersed phase breaks up to produce large drops and simultaneously the drops coalesce to form larger drops. The drop breakage rate dominates the drop coalescence rate in the initial stage of stirring, which causes the drop sizes to decrease with time (Narishman *et al.*, 1980). As stirring proceeds, the drop breakage rate decreases while drop coalescence rate increases. Ultimately, a steady state is reached where the rate of both processes become equal, and a steady-state drop size distribution is established.

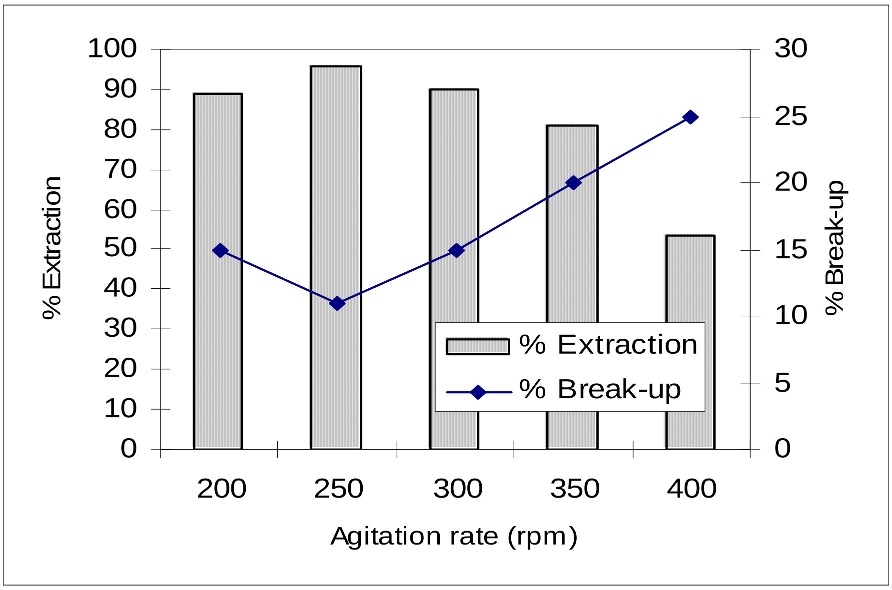


Figure 5.19: Effect of agitation speed on silver extraction and break-up of emulsion (Experimental conditions: Extraction time = 7.5 min, TR = 1:5, [Span 80] = 5 % (w/v), feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M HCl, and diluent = kerosene).

5.4.3 Effect of Liquid Membrane Composition

Both the stability of the emulsion and the viscosity of the liquid membrane were altered by the proportion of surfactant and carrier in the organic phase as reported in Chapter 4. Increasing the concentration of surfactant will increase the stability of emulsion; however at certain concentration the extraction of solute decreased (Li *et al*., 1997). It has been shown that membrane stability is crucial to the efficiency of the ELM. This is true for both membrane swell and membrane breakage. Before the effects of other parameters were elucidated, it was desired to optimize the membrane formulation with respect to the reagents and concentrations. The surfactants most commonly used in ELM formulations is SPAN 80 and polyamine surfactant as reviewed in Table 2.4 but in this work SPAN 80 was the only surfactants tested.

Simple batch experiments were conducted in which only the concentration of surfactant was changed. At the end of each experiment (7.5 minutes contact time) the percent of silver extracted and the change in emulsion volume were calculated. It was observed that increasing the concentration of surfactant, decreases the rate of emulsion breakage but no swelling was observed which indicates that the rate of emulsion breakage is higher than the rate of swelling during the extraction process.

Although no quantitative conclusion can be drawn from the data, several qualitative observations can be made. The negative net change in emulsion volume for essentially all concentration of SPAN 80 indicates a significant breakage of the membrane, as a result of very high swelling and breakage rate. This breakage results in uniformly poor separations.

However, as expected the degree of break-up will approach a constant value due to the saturation of surfactants at the interface. It is also well-known that a surfactant significantly affects the extraction rate of metal ions by ELMs because the complex formation between a carrier and metal ions takes place on the surface of emulsion globules where surfactants adsorb. On the basis of the results in Figure 5.20, the extraction rate of silver is found to decrease with increasing surfactant concentration from 5% to 7% because the adsorption of carrier at the reaction interface inhibits the mass transfer and the effective concentration of carrier for reacting with silver decreases.

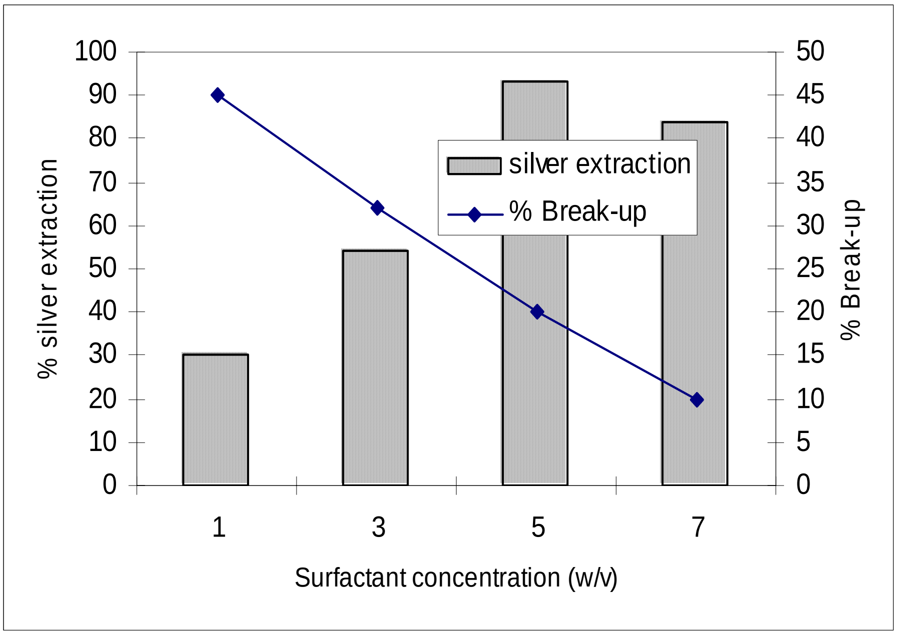


Figure 5.20: Effect of surfactant concentration and break-up of emulsion (Experimental conditions: agitation speed = 250 rpm, TR = 1:5, [Span 80] = 5% (w/v), feed phase = real photographic waste, extraction time = 7.5 min, stripping phase = 1 M thiourea in 1 M HCl, and diluent = kerosene).

5.4.4 Effect of Different Type of Stripping Agent

As discussed in the above section, the main factor in emulsion liquid membrane applicability is stability of emulsion. Apart from agitation speed, carrier and surfactant concentration another parameter is stripping agent types. Figure 5.21 shows the effect of different acid type of thiourea solution on emulsion swelling and breakage. The results indicate that acid sulfuric is more preferable in making acidic thiourea solution where the emulsion is almost stable during the extraction process and no breakage was observed. However the swelling increases with time within 10 minutes, but after that some of emulsion globules start to break-up while the water transport still arise to the others emulsion droplets. This phenomenon was illustrated in Figure 5.22. One globule consists of several tens of droplets. After a few minutes, the droplets size increased as illustrated in Figure 5.22(b), caused by water transport from the external to inside the emulsion droplets. According to

Thien and Hatton (1988), the droplets at the edge of the globule expand to roughly twice their initial size. These increasing sizes of droplet, makes the edge of some droplets to attach to each other and some touched the edge of emulsion globule, subsequently the globule tends to swell and the volume of internal phase increases until the emulsion globules starts to brake. As a result, the water transfer to the external phase and the volume of emulsion phase decreased. It is also acknowledged that emulsion with bigger droplets sizes are subject to higher incidences of breakage (Takahashi *et al.*, 1981).

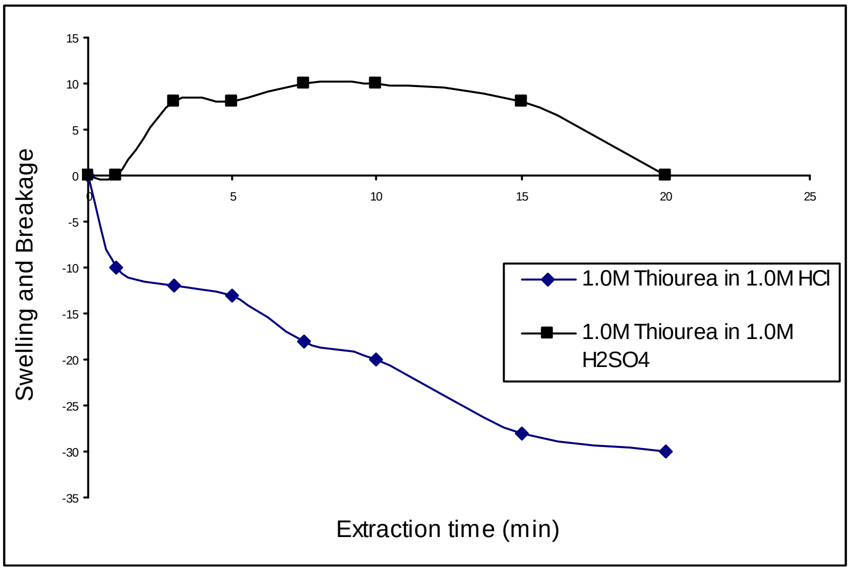


Figure 5.21: Effect of different acid types on apparent swelling of emulsion (Experimental conditions: Agitation speed = 250 rpm, TR = 1:5, [Span 80] = 5% (w/v), feed phase = real photographic waste, extraction time = 7.5 min, stripping phase = 1 M acidic thiourea, and diluent = kerosene).

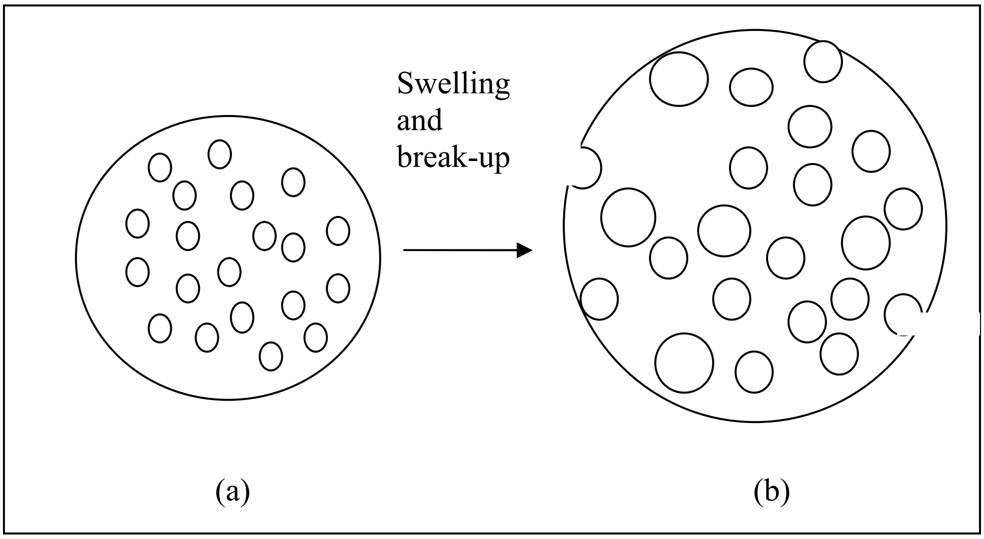


Figure 5.22: Swelling and Break-up phenomena in W/O/W emulsion.

On the other hand, the mechanisms of globule breakage have been studied by Rumscheidt and Mason (1961) and Srinivasan and Stroeve (1986) and have been shown be primarily that due to necking of the globule as discussed in Chapter 4. The globule deforms into a dumbbell shape. The narrow portion, either due to extreme stretching or turbulence-induced surface wave, becomes so thin that the droplets in this portion are to large to be covered by the oil. These droplets are then ejected into the continuous phase.

5.4.5 Effect of Extraction Time

Figure 5.23 shows a slight increase in the interior phase volume as a function of residence time. The exterior phase profile which is presented by the amount of silver extracted indicates no further separation was achieved after 3 minutes. Beside this, the silver transport was most likely masked the net decrease in the external phase volume due to swell minus the breakage volumes. This decrease would increase the external phase concentration, as shown that the amount of silver remaining in the external phase increase after 5 minutes. As expected, in this studies both breakage and swell increases significantly as a function of residence time. This finding supported by Kopp *et al.*, (1978) and Thein *et al.*, (1988) shows that the percentage of swelling generally increases linearly with the square root of time after an initial nonlinear period. Hong and Lee (1983) indicated that the average drop size during the initial period of mixing decreases exponentially while the size distribution changes less drastically from wide to narrow. The minimum transition time was found to depend on the mixing and system's physical properties (Hong and Lee, 1985). From the experimental observation it was found that the size of emulsion globules is big at initial stage and become smaller after 10 minutes extraction process.

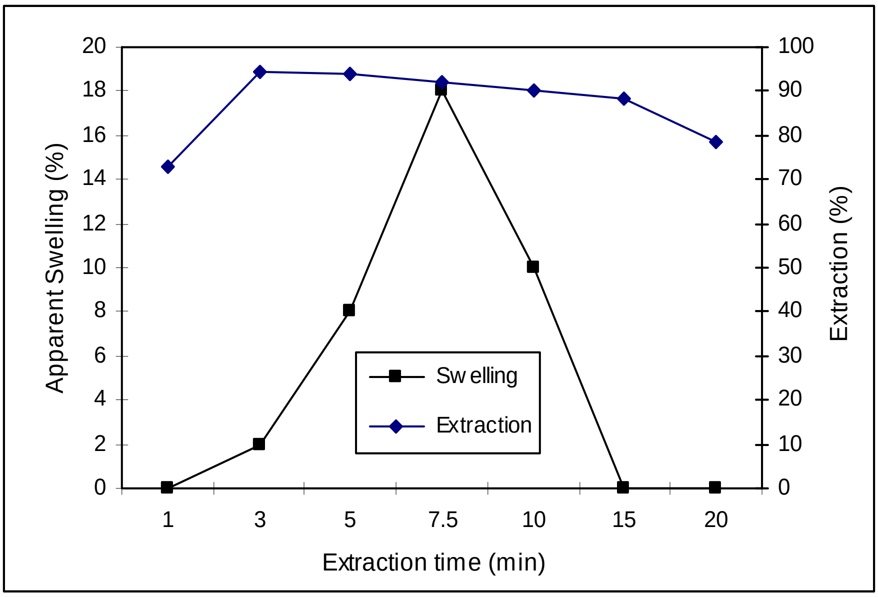


Figure 5.23: Effect of extraction time on silver extraction and apparent swelling. (Experimental conditions: [Cyanex 302] = 0.05 M, TR = 1:5, [Span 80] = 5 % (w/v), agitation speed = 300 rpm, feed phase = real photographic waste, stripping phase = 1 M thiourea in 1 M H_2SO_4, and diluent = kerosene).

It should be noted that during the extraction process, swell and breakage occurred at approximately the same time, which in water solute are transported from the external phase to the internal phase while the emulsion gradually undergoes breakage. As a result, the swell caused the dilution of the internal phase and the breakage caused the decrease in the system efficiency, since the solute which was once separated in the internal phase is released back to the external phase.

The result also shows that the swell increased with the increase in the total contact time until it reached the critical point at minute 5, then the swollen emulsion was spill out. As a result the volume of internal phase decreased at 7.5 minutes. It means the mass volume was transfer from the internal to the external phase.

5.5 Emulsion Liquid Membrane Recovery Process

One benefit of ELM processes is recyclable liquid membrane, which means the emulsion must be demulsified back for product recovery and also liquid membrane recycling. In this system of silver recovery from photographic wastes, a few parameters have been studied on their effect of recovery process such as carrier concentration, stripping agent concentration and treat ratio. The demulsification process of emulsion liquid membrane was done by using batch high voltage demulsifier system. This emulsion demulsified until organic and aqueous phases were clearly separated.

5.5.1 Effect of Carrier Concentration

Carrier concentration plays an important role in the silver recovery process. As discussed, the carrier-metal complexes will release the metal at membrane-internal interface and it will diffuse back to the external-membrane interface. This task illustrates that only a little carrier is required for transporting the metal. Table 5.9 shows that by increasing Cyanex 302 concentration from 0.01 M to 0.04 M, the percentage of silver recovery increased to 100% but further increase to 0.05 M the percentage drop down to 38%. It is because the membrane was concentrated with metal-carrier complexes and does not release it to the internal phase. This crowding will affect resist metal transport process that lead to a decrease in the percentage of stripping process. On the other hand, high concentration of Cyanex 302 will reduce the liquid membrane viscosity and affect the stability of emulsion as discuss before. This effect is deduced by the amount of silver remaining in the external phase.

Therefore, the carrier concentration is an important factor, which is beneficial up to certain limit but in excess it will destroy the process efficiency. This finding indicates that since the liquid membrane was not saturated with carrier-metal complexes, the stripping process functions to strip silver into the receiving phase.

Table 5.9: Effect of cyanex 302 concentration on silver recovery in ELM system (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 3% (w/v), treat ratio = 1:5, feed phase = real photographic wastes, and stripping phase = 1 M thiourea in 1 M H_2SO_4).

[Cyanex 302] (M)	$[Ag_{ext}]_{initial}$ (ppm)	$[Ag_{ext}]_{final}$ (ppm)	$[Ag_{int}]$ (ppm)	$[Ag_{mem}]$ (ppm)	% S	% R
0.01	2824	557	13165	9501	58	47
0.02	2824	378	23190	1268	95	82
0.03	2824	210	31435	0	100	100
0.04	2824	172	28530	0	100	100
0.05	2824	282	10725	14692	42	38

5.5.2 Effect of Stripping Agent Concentration

Concentration of thiourea and acid solution plays an important role in the first extraction process as discussed in Section 5.2.2. Actually, this extraction performance was influenced by strip agent solution. If the diffused Ag-Cyanex 302 complexes cannot strip because of the lack of the strip agent, these complexes will accumulate in the membrane phase and ELM process was denied. On the other hand, the remaining silver in the external phase is quite high because of emulsion breaking, which leads to silver-thiourea in the internal phase to come into the external phase. However, increasing thiourea concentration increased silver recovery almost completely.

Table 5.10: Effect of stripping agent concentration on silver recovery in ELM system (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 3% (w/v), [Cyanex 302] = 0.03 M, treat ratio = 1:5, and feed phase = real photographic waste).

[Thiourea] (M)	[$Ag_{initial}$] (ppm)	[Ag_{final}] (ppm)	[Ag_{int}] (ppm)	[Ag_{mem}] (ppm)	% S	% R
0.25	3230	2420	2730	5380	34	8.5
0.50	3230	1500	13600	3770	78	42.0
0.75	3230	224	38300	0	100	100.0
1.00	3230	223	52100	0	100	100.0
1.50	3230	117	78000	0	100	100.0

5.5.3 Effect of Treat Ratio

Table 5.11 shows the effect of silver recovery with respect to the ratio of emulsion volume to the external phase. Increasing the external phase volume will decrease the recovery efficiency because of the effect of lower extraction efficiency of silver from the external phase. The data presented in Table 5.11 shows that the amount of silver extracted was completely stripped into the receiving phase. The phenomena of long distance diffusion of solute transport, hydrodynamic effect, and stability of emulsion globules that have been discussed in a previous section give significant effect to silver recovery. It is also indicated, the concentration of carrier used must be appropriate to the treat ratio. Thus, the recovery percentage was expected to increase with increasing carrier concentration.

Table 5.11: Effect of treat ratio on silver recovery in ELM system (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 3% (w/v), [Cyanex 302] = 0.02 M, feed phase = real photographic waste, and stripping phase = 1 M thiourea in 1 M H_2SO_4).

Treat ratio emulsion : feed	[Ag $_{\text{initial}}$] (ppm)	[Ag$_{\text{final}}$] (ppm)	[Ag$_{\text{int}}$] (ppm)	[Ag$_{\text{mem}}$] (ppm)	% S	% R
1 : 3	2610	30	29900	0	100	99
1 : 4	2610	262	29800	0	100	90
1 : 5	2610	163	23200	0	100	82
1 : 6	2610	1150	21000	0	100	56
1 : 7	2610	1500	20600	0	100	43

5.6 ELM Transport Mechanism of Silver

The ELM process involves simultaneous extraction and stripping in one step. Although the selective extraction of silver from thiosulfate solutions has not been exhaustively investigated because of tight binding between silver and thiosulfate ions (Mendoza *et al.*, 1996), silver in the form of thiosulfate anionic complex Ag $(S_2O_3)_2^{3-}$ can be removed from the photographic processing solution or photographic waste (Rohm and Haas, 2003). This study also proved the capability of Cyanex 302 and Thiuram as an extractant as discussed in Chapter 4. In the presence of thiosulfate in the photographic wastes solution (Pro-ACT, 1995), the reduction of Cyanex 302 in the membrane phase and formation of the silver-carrier complex occurs according to the reaction below:

$$Ag(S_2O_3)_2^{3-} + \overline{(RH)}_2 \leftrightarrow \overline{Ag(RH)R} + 2(S_2O_3)^{2-} + H^+ \qquad (5.6)$$

From Equation 5.6, it is considered that only one mole of Cyanex 302 is required for forming the silver-extractant complex. The actual stoichiometry in this reaction was shown in Chapter 4 (Section 4.3.1).

The silver-Cyanex 302 complex transfers across the membrane phase and react with the acidic thiourea in the internal phase at the internal interface as in the following reaction:

$$\overline{Ag(RH)R} + CS(NH_2)_2H^+ \leftrightarrow \overline{(RH)_2} + Ag(CS(NH_2)_2)^+ \qquad (5.7)$$

A possible scheme for the silver transport from the feed solution to the internal phase through Cyanex 302-Span 80-kerosene liquid membrane can be shown in Figure 5.24.

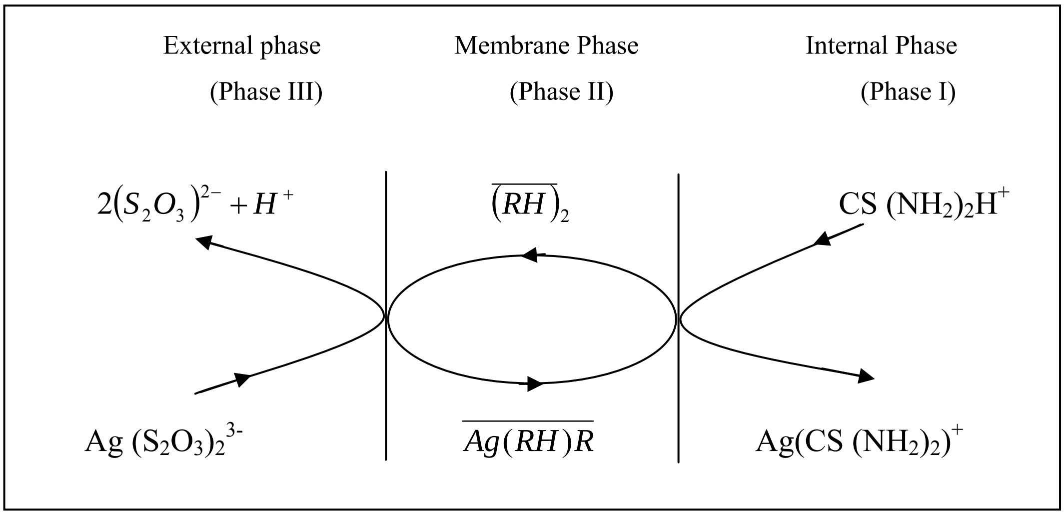


Figure 5.24: A simultaneous extraction and stripping mechanism in ELM extraction process.

5.7 Future Prospects of ELM Process

5.7.1 A ELM Recycling Process

The membrane phase and the internal phase can be separated with high electric forces. The emulsion, which is rich in silver inside the internal phase, was demulsified and separated by applying high voltage electric field. As reported, the membrane phase will be recycled and used again in the emulsification operation.

Figure 5.25 shows the capability of using recycled ELM in the extraction of silver from photographic wastes. The results show that about 85% of silver was extracted using the recycled ELM for 10 minutes process. It is due to the purity of liquid membrane marked by the remaining of unstripped complexes in the membrane phases. In addition, the emulsion liquid membrane made from the recycled organic mixture is less stable after 10 minutes compared to the fresh emulsion. It is observed during the extraction process that the percentage of emulsion breakup is relatively high for long extraction time. On the other hand, Lee (2004) reported the degree of emulsion breakage is very closely related to the emulsion droplet aging. Therefore, one of the key points in recycling the used ELMs was breaking emulsion droplets immediately after the extraction process. However, as reported in the literature, usually it can be recycled once (Abou-Nemeh and Van Peteghem, 1993).

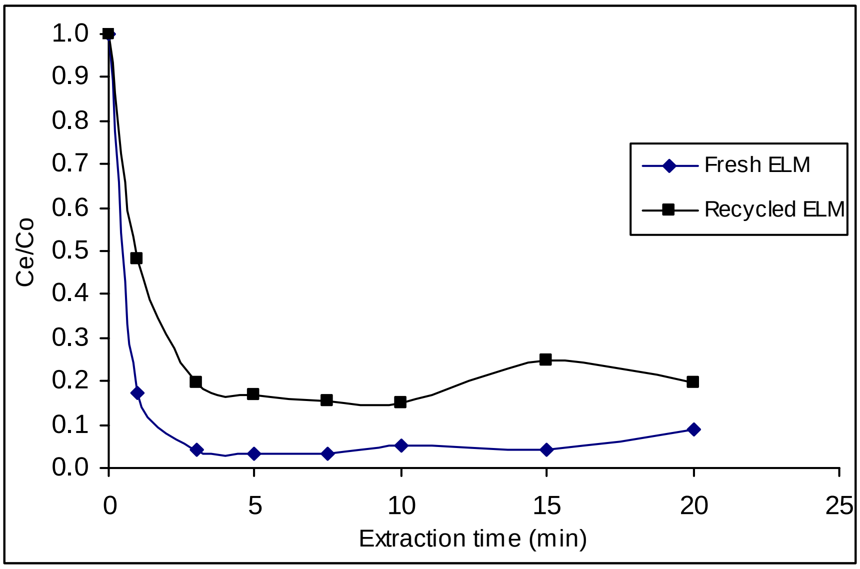


Figure 5.25: Silver extraction in recycling ELM system (Experimental conditions: agitation speed = 250 rpm, [Span 80] = 3% (w/v), [Cyanex 302] = 0.05 M, feed phase = real photographic wastes, and stripping phase = 1 M thiourea in 1 M H_2SO_4).

5.7.2 A Continuous ELM Extraction Process

Emulsion liquid membrane process was carried out in a batch to perform the ability of the system to separate and recover silver from photographic wastes. In this laboratory work, the screening process and parameters studied have been attempted to elucidate the ELM potentials. On the basis of these results, the optimum conditions of liquid membrane formulation and conditions of the batch system can be used as a guide to set-up a continuous process in pilot and industrial processes. Figure 5.26 shows the schematic diagram of propose continuous process mixer settler of ELM. This thesis only experiment with a few aspects of the continuous process system such as a capability of silver recovery and possibility to recycle the liquid membrane by using step by step process. In this experiment, agitated continuous phase was taken out and allowed for phase separation, while a same amount of fresh continuous phase and recycling emulsion liquid membrane was added to the system at the same treat ratio.

The results show that for 5 minutes extraction using 0.03 M Cyanex 302, the extraction percentage decrease from 92.6% to 52.5% for triple ELM recycling. It is due to unstability of emulsion globules during the process. From experimental observation, the final volume of emulsion after extraction decreases which means that the emulsion was broken and the solute in internal phase was transferred to external phase. Actually the extraction is still good enough but because of its unstability the system potential departed. Another factor is the liquid membrane component impurity which refers to the amount of extracted silver remaining in the liquid membrane as illustrated in Figure 5.27. If this disturbance happen to the system, meaning that the Cyanex 302 complexes in liquid membrane diminish recycling process. However, the stripping potentials of about 95% are considered satisfying to the ELM recycling system. On the other hand, recovery percentage of 61% and 50% for second and third cycle are considered high compared with using the fresh emulsion.

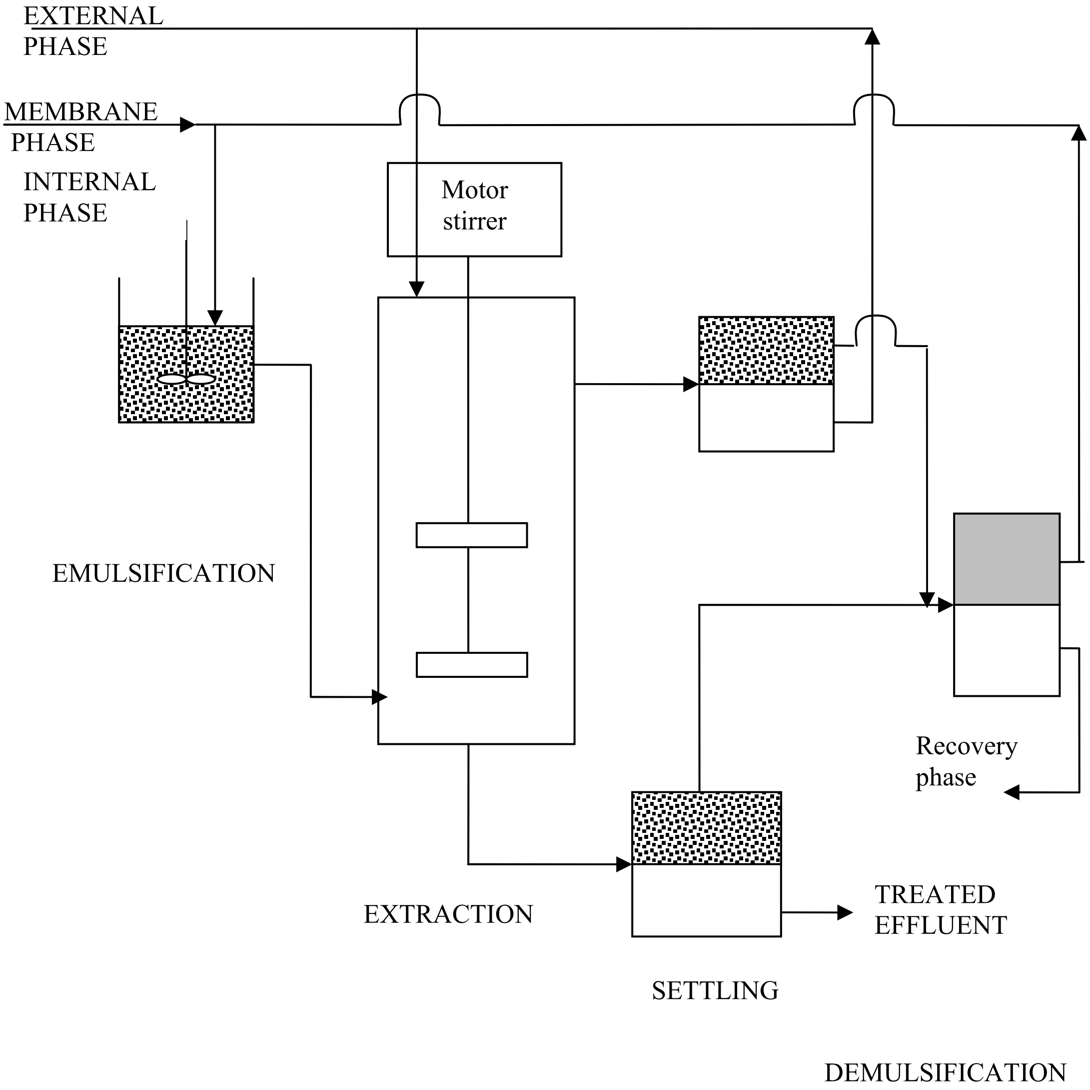
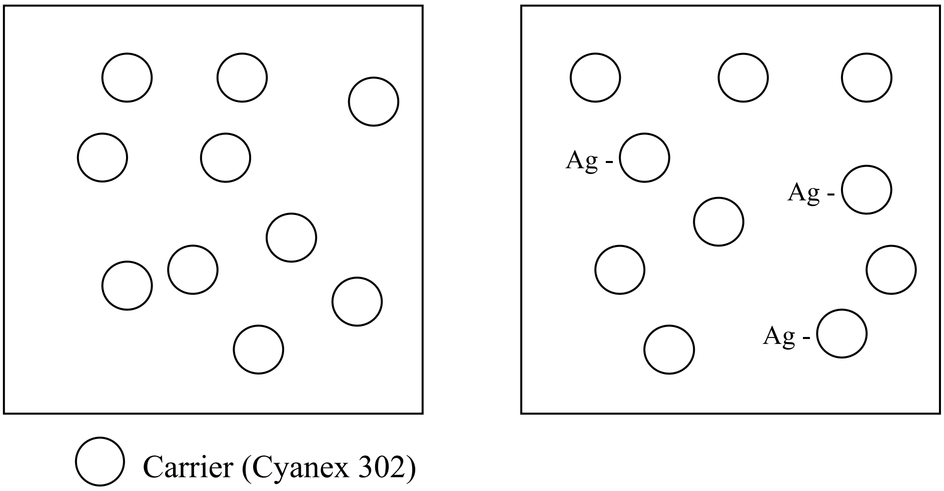


Figure 5.26: A schematic diagram of proposed continuous ELM extraction system.



(a) Fresh liquid membrane (b) Recycle liquid membrane

Figure 5.27: A schematic diagram of fresh and used liquid membrane component.

For future prospect of continuous process, the following suggestion should be made. Recycling of ELM is very promising if the system has not excesses with carrier and it has enough extraction time which is the solute in the external phase is almost completely extracted and stripped into the internal phase. Therefore, the recycling liquid membrane must be free from any metal complexes where it will act as fresh carrier but a precaution should be taken for emulsion stability. It is due to the surfactant distortion during the extraction and demulsification process. On the other hand, from experimental observation, recycling liquid membrane is not totally phase separated based on the turbid colour of the liquid membrane. Therefore, this demulsified liquid membrane must be allowed to undergo phase separation for at least one day before reusing it. This promising result was shown in Figure 5.25. In contrast, direct use of liquid membrane will cause the extraction efficiency to be relatively low as shown in Table 5.12. To maintain the efficiency of liquid membrane, the emulsified liquid membrane from settling tank can be mixed with fresh liquid membrane as proposed in Figure 5.26.

Table 5.12: Liquid membrane potential in continuous ELM system (Experimental condition: agitation speed = 250 rpm, [Span 80] = 3% (w/v), [Cyanex 302] = 0.03 M, feed phase = real photographic waste, extraction time = 5 minutes, and stripping phase = 1 M thiourea in 1 M H_2SO_4).

ELM Stage	$[\text{Ag}_{\text{initial}}]_{\text{ext}}$ (ppm)	$[\text{Ag}_{\text{final}}]_{\text{ext}}$ (ppm)	$[\text{Ag}]_{\text{int}}$ (ppm)	$[\text{Ag}_{\text{mem}}]$ (ppm)	%E	% S	% R
1	2660	212	23600	834	92.6	96.5	88.8
2	2660	930	16200	3100	65.0	93.6	60.9
3	2660	1262	13310	660	52.5	95.3	50.1

5.8 Summary

Emulsion liquid membrane extraction of silver from photographic wastes becomes one of the promising techniques in silver recovery process. Silver was almost completely extracted from photographic wastes using ELM extraction process under certain process conditions under study. In this process carrier and strip agent types and concentration plays an important role. Therefore, Cyanex 302 and thiourea in sulfuric acid solution provides good capability in extracting silver from complex solution of liquid photographic wastes. Other parameters influencing the process are concentration of emulsifier, size of emulsion, process agitation speed, and treat ratio of emulsion to feed phase. In addition, to maintain the emulsion stability a few parameters that affect the membrane breakage have been studied such as liquid membrane composition, strip agent and agitation speed. If all these parameters are utilized in correct conditions with proper equipment selection, silver can be extracted and recovered completely from photographic wastes.

CHAPTER 6

MODELING OF LIQUID MEMBRANE EXTRACTION OF SILVER

6.1 Introduction

An emulsion liquid membrane system has been shown to successfully extract silver from liquid photographic wastes. A mathematical model will established to simulate the extraction of silver in order to compare with the experimental results. A mathematical model will be developed based on general ELM model with a few assumptions and modification. Usually, the Type 2 facilitated transport can be introduced based on either spherical shell or emulsion globules models as discussed in Chapter 2. However, the emulsion globule approach is more appropriate compared to spherical shell approach. Therefore, in developing silver extraction model, it will consider emulsion globule approach and this model also will consider the emulsion breakage during the ELMs process. In this study, ELMs model will be developed and solved numerically.

6.2 ELM Batch Extraction Model

6.2.1 Preliminary Study

The theory of ELM extraction modeling has been investigated by many workers. Lorbach and Marr (1987) developed a model of zinc extraction for Type 2 facilitation transport mechanism. In this model they took into account the diffusion of carrier and carrier-solute complex in the membrane globules and the reversible reactions at the external and internal interfaces. Although some simplifications have been made on constant summation of free and complex carrier, constant pH in the external phase and eliminated resistance for the peripheral thin membrane, based on Teramoto *et al*. (1983) and Kataoka (1989) model, there were still four parameters dealing with extraction and stripping equilibrium that are quite difficult to determine correctly in this study.

Lee *et al*. (1996) developed a general physical model which is good for silver extraction. However, it made a simplification that the mass transfer resistances of silver and hydrogen ions in the external aqueous phase were neglected. Wang (1984) showed that the external phase resistances cannot be neglected. However, it is reported that for ELM system with adequate mixing speed which produced well mixed globules, the external mass transfer resistance is not significant compared with the resistance from the diffusion of the solute/carrier complex (Stroeve and Varanasi, 1984). Since the agitation rate in this system was quite high, external resistance was assumed insignificant and can be neglected. On the other hand, it is interesting to know that Rajdip *et al*. (1998) developed a new model of batch-extraction in emulsion liquid membrane considering interaction of globules for the Type I facilitation mechanism but will not be considered in this model.

This model will consider the leakage of the internal aqueous phase to the external phase due to the membrane breakage and this model also tried to adapt Lee *et al*. (1996) model to make it more flexible. In order to simplify the model, the following assumptions should be made;

i) The diameters of emulsion globules and internal droplets are uniform and can be expressed as the Sauter mean diameter.
ii) The internal aqueous phase droplets are immobile and so there is no circulation of the droplets within the emulsion drop.
iii) The ionic form of the solute existing in the external phase is insoluble in the membrane phase, so that extraction by non-facilitated transport and diffusion by complexes itself without carrier is negligible.

iv) The physical properties of all the phases and the diffusion coefficient of the solute-carrier complex through the membrane phase are constant throughout the extraction process.

v) The main mechanism of leakage is the mechanical rupture of internal phase droplets at the globule interface.

vi) The volume change of the emulsion liquid membrane phase and the external phase due to leakage can be neglected.

vii) Reaction at external and internal interface a rapidly compared to diffusion rate.

viii) Tank is well mixed at constant temperature conditions

ix) The local reaction at the external interface between the external and the membrane phases is in equilibrium.

x) The mass transfer resistance in the internal aqueous phase is neglected because of very small size of the droplets.

6.2.2 Mathematical Modeling of Transport Process

The model of carrier mediated transport is much more complicated than that of diffusion limited type because extracting reaction and stripping reaction of the solute occur on two liquid-liquid interfaces in the emulsion liquid membrane system. Lorbach and Marr (1987) developed a model of carrier transport type for extraction of zinc with many variables. In order to adopt this model for extraction of silver from photographic wastes some transport mechanism assumptions should be made as the following:

i) diffusion of ion Ag to the surface of the emulsion globules

ii) reaction of ion Ag with carrier at the external interface

iii) diffusion of the silver-loaded carrier into the emulsion globules

iv) stripping of the loaded carrier at the internal interface between the membrane phase and the internal droplet phase

v) back diffusion of the carrier to the interface between the external phase and membrane phase.

Modification of Lorbach and Marr (1987) and Lee *et al.* (1996) models considering membrane breakage during the extraction process was studied in this thesis. The governing equations for the extraction processes are:

a) Mass balance equation in external aqueous phase:

$$-V_{III}\frac{dC_{A,III}}{dt} = k_c S_A (C_c\big|_{r=R} - C_c\big|_{r=Ri}) - M_B C_{A,I}\big|_{r=Ri} \tag{6.1}$$

$$V_{III}\frac{dC_{H,III}}{dt} = k_c S_A (C_c\big|_{r=R} - C_c\big|_{r=Ri}) + M_B C_{H,I}\big|_{r=Ri} \tag{6.2}$$

Where,

$C_{A,III}$: Concentration of solute in the external phase (mol/l).

$C_{H,III}$: Concentration hydrogen ion in the external phase (mol/l).

C_c : Concentration of metal complex at the external-membrane interface (mol/l).

k_c :Mass transfer coefficient through pheripheral layer of membrane (m^2/s).

V_{III} : Volume of external phase (ml)

R : Sauter mean radius of an emulsion globules (m)

M_B : Rate of leakage

S_A : Sphere area of globules emulsion

b) Mass balance of solute-carrier complex (C) within emulsion globules $0 \le r \le R_i$

Interfacial area between membrane and internal droplets;

$$S' = 4\pi R_\mu^{\;2} \tag{6.3}$$

$$V_I = \frac{4}{3}\pi R\mu^3 \tag{6.4}$$

Dividing Equation 6.3 with Equation 6.4;

$$\frac{S'}{V_I} = \frac{4\pi R_\mu{}^2}{{}^4\!/_3\,\pi R_\mu{}^3} = \frac{3}{R_\mu} \tag{6.5}$$

$$S' = \frac{3}{R_\mu} V_I \tag{6.6}$$

$$V_{II}\frac{\partial C_c}{\partial t} = \left(V_I + V_{II}\right)_i D_{ec}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_c}{\partial r}\right)\right) - \frac{3V_I}{R_\mu} r_s \tag{6.7}$$

$$V_{II}\frac{\partial C_c}{\partial t} = \left(V_I + V_{II}\right)_i D_{ec}\left(\frac{\partial^2 C_c}{\partial r} + \left(\frac{2}{r}\frac{\partial C_c}{\partial r}\right)\right) - \frac{3V_I}{R_\mu} r_s \tag{6.8}$$

c) Analogically, mass balance of carrier (B) within emulsion globules $0 \le r \le R_i$ can be expressed by using the effective diffusivities of carrier, D_{eB}.

$$V_{II}\frac{\partial C_B}{\partial t} = \left(V_I + V_{II}\right)_i D_{eB}\left(\frac{\partial^2 C_B}{\partial r} + \left(\frac{2}{r}\frac{\partial C_B}{\partial r}\right)\right) + \frac{3V_I}{R_\mu} r_s \tag{6.9}$$

Where,

V_I : Volume of internal phase (ml)

V_{II} : Volume of liquid membrane phase (ml)

D_{ec} : effective diffusivity of solute-carrier complex in emulsion phase (m^2/s)

D_{eB} : effective diffusivity of carrier in emulsion phase (m^2/s)

C_B : Concentration of metal complex at the external-membrane interface (mol/l).

r_s : Rate of stripping

S' : Sphere area of emulsion droplets

Volume ratio of emulsion globules:

$$\frac{4/3\pi R_i^3}{4/3\pi R^3} = \frac{(V_I + V_{II})_i}{(V_I + V_{II})}$$

$$\left(\frac{R_i}{R}\right)^3 = \frac{(V_I + V_{II})_i}{(V_I + V_{II})} \tag{6.10}$$

Lets β is a parameter for the thickness of the thin oil layer given by the following equation:

$$\beta = 1 - \left(\frac{R_i}{R}\right) \tag{6.11}$$

$$\left(\frac{R_i}{R}\right) = 1 - \beta \tag{6.12}$$

So Equation 6.10 becomes:

$$(1-\beta)^3 = \frac{(V_I + V_{II})_i}{(V_I + V_{II})} \tag{6.13}$$

$$(V_I + V_{II})_i = (V_I + V_{II})(1-\beta)^3 \tag{6.14}$$

Divide Equations 6.8 and 6.9 by $(V_I + V_{II})_i$:

$$\frac{V_{II}}{(V_I + V_{II})(1-\beta)^3}\frac{\partial C_c}{\partial t} = D_{ec}\left(\frac{\partial^2 C_c}{\partial r} + \left(\frac{2}{r}\frac{\partial C_c}{\partial r}\right)\right) - \frac{1}{(V_I + V_{II})(1-\beta)^3}\frac{3V_I}{R_\mu} r_s$$

(6.15)

$$\frac{V_{II}}{(V_I + V_{II})(1-\beta)^3}\frac{\partial C_B}{\partial t} = D_{eB}\left(\frac{\partial^2 C_B}{\partial r} + \left(\frac{2}{r}\frac{\partial C_B}{\partial r}\right)\right) + \frac{1}{(V_I + V_{II})(1-\beta)^3}\frac{3V_I}{R_\mu} r_s$$

(6.16)

Lets ϕ_1 is the volume fraction of the internal phase in emulsion drop, $V_I/(V_I+V_{II})$ and ϕ'_1 is equal to $\phi_1/(1-\beta)^3$, Equations 6.15 and 6.16 become:

$$(1-\phi'_1)\frac{\partial C_B}{\partial t} = \frac{1}{r^2}\left(\frac{\partial}{\partial r} D_{eB} r^2 \frac{\partial C_B}{\partial r}\right) + \frac{3\phi'_1}{R_\mu} r_s \qquad (6.17)$$

$$(1-\phi'_1)\frac{\partial C_C}{\partial t} = \frac{1}{r^2}\left(\frac{\partial}{\partial r} D_{eC} r^2 \frac{\partial C_C}{\partial r}\right) - \frac{3\phi'_1}{R_\mu} r_s \qquad (6.18)$$

d) Mass balance of solute (A) in the internal phase;

$$V_I \frac{dC_{A,I}}{dt} = \frac{3}{R_\mu} V_I r_s \qquad (6.19)$$

$$\phi'_1\left(\frac{dC_{A,I}}{dt}\right) = \frac{3\phi'_1}{R_\mu} r_s \qquad (6.20)$$

where $3\phi'_1/R_\mu$ corresponds to the interfacial area between the membrane phase and the internal phase per unit volume of the (W/O) emulsion phase. In addition, the following relation holds in the internal phase and is assumed to be equivalent to ELM silver extraction system:

$$eC^0_{A,I} + C^0_{H,I} = eC_{A,I} + C_{H,I} \tag{6.21}$$

Initial and boundary conditions (ICs, BCs) are respectively expressed as follows:

Initial conditions(IC):

For t = 0: $C_{A,III} = C^o_{A,III}, C_{H,III} = C^o_{H,III}$

For t = 0, $0 \le r \le R_i$: $C_B = C^o_B, C_C = 0, C_{A,I} = C^o_{A,I}, C_{H,I} = C^o_{H,I}$ (6.22)

Boundary conditions (BC);

For $\mathrm{t} \ge 0, \mathrm{r} = 0$: $\frac{\partial C_B}{\partial r} = 0, \frac{\partial C_c}{\partial r} = 0$ (6.23)

For $\mathrm{t} \ge 0, \mathrm{r} = \mathrm{R_i}$:

$$\left(-D_{eB}\left(\frac{\partial C_B}{\partial r}\right) + \phi_1^{2/3} r_s \right)_{r=Ri} \tag{6.24}$$

$$= \left(D_{eC}\left(\frac{\partial C_B}{\partial r}\right) + \phi_1^{2/3} r_s \right)_{r=Ri}$$

$$= k_B\left(C_B\big|_{r=Ri} - C_B\big|_{r=R}\right)$$

$$= k_C\left(C_C\big|_{r=R} - C_C\big|_{r=Ri}\right)$$

$$= r_f\big|_{r=R}$$

where,

k_B and k_C are the mass transfer coefficients of B and C in the peripheral thin oil layer respectively. ϕ_1 is the volume ratio of the internal phase in the emulsion drop.

e) Recovery efficiency, E

The recovery efficiency is defined as:

$$E(t) = 1 - \frac{C_e(t)}{C_{eo}} \tag{6.25}$$

6.2.3 Numerical Solution

The above set of basic equations (Section 6.2.2) results in a non-linear partial difference equation system, which was solved by the numerical method of lines approach. This technique is based on discretisation of the spatial derivative transforming each partial differential equation into a system of ordinary differential equations. Figure 6.1 shows the radius of the emulsion globules is separated into n intervals or (n+1) points. Based of this illustration, Equations 6.15 and 6.16 were derived numerically as the following using centered finite difference method.

$$D_{eB}\left(\frac{\partial^2 C_B}{\partial r} + \left(\frac{2}{r}\frac{\partial C_B}{\partial r}\right)\right)$$

$$= D_{eB}\left[\frac{1}{\Delta r^2}\left(C_{i,j+1} - 2C_{i,j} + C_{i,j-1}\right) + \frac{2}{r}\frac{(C_{i,j+1} - C_{i,j-1})}{2\Delta r}\right]$$

$$= D_{eB}\left[\frac{1}{\Delta r^2}\left(C_{i,j+1} - 2C_{i,j} + C_{i,j-1}\right) + \frac{1}{r\Delta r}(C_{i,j+1} - C_{i,j-1})\right]$$

$r = j\Delta r$

$$= D_{eB}\left[\frac{1}{\Delta r^2}\left(C_{i,j+1} - 2C_{i,j} + C_{i,j-1}\right) + \frac{1}{j\Delta r^2}(C_{i,j+1} - C_{i,j-1})\right] \tag{6.26}$$

where,

i = 0,1, 2, 3 …N

j = 0, 1, 2, 3…N

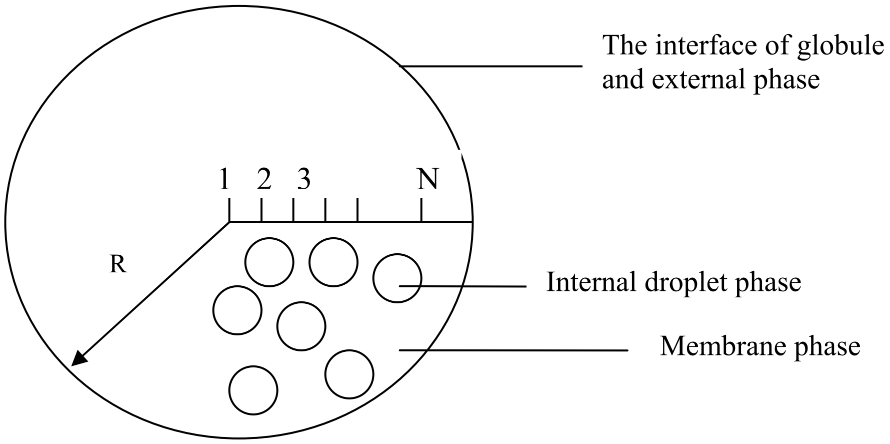


Figure 6.1: Numerical analysis consideration in emulsion globule.

Substituting Equation 6.23 into Equations 6.17 and 6.18 yield;

$$(1-\phi'_1)\frac{\partial C_c}{\partial t} = D_{eC}\left[\frac{1}{\Delta r^2}\left(C_{Ci,j+1} - 2C_{Ci,j} + C_{Ci,j-1}\right) + \frac{1}{j\Delta r^2}(C_{Ci,j+1} - C_{Ci,j-1})\right] - \frac{3\phi_1'}{R_\mu} r_s \tag{6.27}$$

$$(1-\phi'_1)\frac{\partial C_B}{\partial t} = D_{eB}\left[\frac{1}{\Delta r^2}\left(C_{Bi,j+1} - 2C_{Bi,j} + C_{Bi,j-1}\right) + \frac{1}{j\Delta r^2}(C_{Bi,j+1} - C_{Bi,j-1})\right] - \frac{3\phi_1'}{R_\mu} r_s \tag{6.28}$$

Equations 6.27 and 6.28 are only valid when r ≠ 0. For r = 0, Equation 6.17 become:

$$(1-\phi'_1)\frac{\partial C_B}{\partial t} = \frac{1}{r^2}\left(\frac{\partial}{\partial r} D_{eB} r^2 \frac{\partial C_B}{\partial r}\right) + \frac{3\phi'_1}{R_\mu} r_s$$

$$= D_{eB}\left(3\frac{\partial^2 C_B}{\partial r^2}\right) + \frac{3\phi'_1}{R_\mu} r_s$$

$$= D_{eB}\left(6\frac{C_{B,1} - C_{B,0}}{\Delta r^2}\right) + \frac{3\phi'_1}{R_\mu} r_{s,0} \tag{6.29}$$

For r = 0, Equations 6.18 become:

$$(1-\phi'_1)\frac{\partial C_C}{\partial t} = \frac{1}{r^2}\left(\frac{\partial}{\partial r} D_{eC} r^2 \frac{\partial C_C}{\partial r}\right) - \frac{3\phi'_1}{R_\mu} r_s$$

$$= D_{eC}\left(6\frac{C_{C,1} - C_{C,0}}{\Delta r^2}\right) - \frac{3\phi'_1}{R_\mu} r_{s,0} \tag{6.30}$$

On the other hand, the equations at the boundaries would have to be modified according to the boundary conditions in Equation 6.24.

$$\left(\frac{\partial C_B}{\partial r}\right)_{r=Ri} = \frac{k_B}{D_{eB}}\left(C_B\big|_{r=R} - C_B\big|_{r=Ri}\right) = \frac{1}{2\Delta r}\left(C_{B,N+1} - C_{B,N-1}\right)$$

$$C_{B,N+1} = \frac{2k_B\Delta r}{D_{eB}}\left(C_B\big|_{r=R} - C_B\big|_{r=Ri}\right) + C_{B,N-1} \tag{6.31}$$

$$\left(\frac{\partial C_C}{\partial r}\right)_{r=Ri} = \frac{k_C}{D_{eC}}\left(C_C\big|_{r=R} - C_C\big|_{r=Ri}\right) = \frac{1}{2\Delta r}\left(C_{C,N+1} - C_{C,N-1}\right)$$

$$C_{C,N+1} = \frac{2k_C\Delta r}{D_{eC}}\left(C_C\big|_{r=R} - C_C\big|_{r=Ri}\right) + C_{C,N-1} \tag{6.32}$$

where r = R_i = N = the point at the radius of inner core of W/O emulsion drop. $C_B\big|_{r=R}$ and $C_C\big|_{r=R}$ can be calculated by the equilibrium relation at the external interface between the external aqueous phase and the membrane phase.

These systems of equations of Equation 6.1, 6.2, 6.20, 6.27, 6.28, 6.29 and 6.31 using the conditions of Equations 6.22 – 6.24 were solved simultaneously by Runge-Kutta forth degree using MATLAB software as shown in Appendix F.

6.2.4 Model Parameters Estimation

In this model, some parameters are based on the experimental conditions as well as from empirical correlations. In addition, parameters like D_m, D_{eff}, K_{eq} and R can be obtained from certain equations available in the previous paper or directly from experiments. The methods to obtain these parameters are discussed in the following section. Typical modeling parameters are shown in Table 6.1.

Table 6.1: Typical parameters of the batch extraction model.

Experimental Parameters:

Silver concentration, C_{eo}	= 2600 ppm
Carrier concentration, C_{Bo}	= 0.05 M
Acidic thiourea concentration, C_{Ho}	= 1.0 M
Treat ratio,TR	= 1:5
Volume fraction internal in emulsion drop	= 1:1

Equilibrium Constant and Relative Diffusivities:

K_{eq} = 1.16

k_C = 0.0022 m/s

D_{eC} = 2.312×10^{-9} m^2/s

k_s = 1.5×10^{-8} $m^4/mol.s$

R = 5×10^{-4} m

R_m = 3.31×10^{-6} m

6.2.4.1 Effective Diffusivity and Mass Transfer Coefficient

To elucidate the mechanism of the ELM extraction, the analysis of diffusion process within the emulsion drop is crucial; in particular, effective diffusivity of solute in a (W/O) emulsion drop is one of the important parameters for modeling the permeation of the solute through ELMs. Several expressions for evaluating the effective diffusivity have been proposed (Ho and Li, 1992).

In the immobilized globule model, being one of geometric models for (W/O) emulsion drops, the internal aqueous droplets are assumed to be distributed uniformly in the drop and not to be mixed with each other. There are some models for evaluating effective diffusivity in (W/O) emulsion drops; however, the models have not taken mass-transfer resistance through the interface between the internal aqueous and membrane phases into consideration. A permeation model for (W/O) emulsion drop was presented by extending the cubic model derived by Teramoto and Matsuyama (1986) as illustrated in Appendix C.

Because the emulsions are composed of organic membrane phases and internal phases, the effective diffusivity in emulsion globules should be calculated from consideration of diffusivities in membrane and internal phases. The final equation of the effective diffusivity is defined by;

$$D_{eC} = D_C\left[\frac{1}{\phi_1^{-1/3} - \phi_1^{1/3} + \frac{k_s C_H}{D_C}\phi_1^{1/3}\left(\frac{4}{3}\pi R_\mu^{\ 3}\right)^{1/3}} + 1 - \phi_1^{1/3}\right]^{-1} \qquad (6.33)$$

The effective diffusivity, D_{eB} was assumed to be equal to D_{eC} because the molecular diffusivity of silver complex was almost equal to that of carrier. D_C and stripping coefficient, k_s were determined by optimization. The value of effective diffusivity is 2.312x 10^{-9} m^2/s.

The thickness, δ of the thin oil layer is considered to be equivalent to the thickness $l-d$ of the oil membrane phase surrounding the internal aqueous droplet. The dimension of l is calculated from the size of the internal droplets and the fraction of internal phase in emulsion drop. Thus, the thickness of thin oil layer is expressed by

$$\delta = l - d = (4\pi / 3)^{1/3} R_{\mu} \left(\phi^{-1/3} - 1\right) \qquad (6.34)$$

Hence, the mass transfer coefficient k_C and k_B in the thin oil layer are given by

$$k_C = \frac{D_C}{\delta}, k_B = \frac{D_B}{\delta} \ = \ 0.0022 \text{ m/s} \qquad (6.35)$$

6.2.4.2 Emulsion Droplet Sauter Mean Diameter

For the determination of the globules emulsion size, sauter mean diameter is being used. The Nikon camera with Video Structure Image Analyzer was used for this measurement. The result found that, at typical condition of 200 and 250 rpm, the size of emulsion globules are 1.5 mm and 1.0 mm respectively. However, it was very difficult to take a clear picture at a speed rate 300 and 350 rpm. It is because the emulsions are very small and move faster during the extraction process. As a result, these pictures are unsuccessful determine in image analyzing process. Therefore, at these levels of stirring rate, Reis and Carvalho (2004) correlation (Appendix D) was used to predict the size of emulsion globules which is the Sauter mean diameter of emulsion globules is proportional to $N^{-1.4}$. Table 6.2 shows the sizes of emulsion globules at different speed of stirring rate based on this correlation. Meanwhile, the internal aqueous droplets were measured by the photographic method. In this case, microscopic picture was taken and analyzed with the Video Structure Image Analyzer. The respective Sauter mean diameter was obtained is 3.31×10^{-6} m.

Table 6.2: Size of emulsion droplets based on Reis and Carvalho (2004) correlation.

Stirring rate (rpm)	Sauter mean diameter (d_{32}) (mm)

300	0.3 - 0.4
350	0.2 - 0.3
400	0.1 – 0.2

6.2.4.3 Equilibrium Constant

The kinetics of silver extraction with Cyanex 302 was investigated. It is difficult to find the equilibrium constant for extraction reaction from the literature. Hence, experiments should be done for obtaining this constant. The experimental procedures were shown in Appendix E. According to extraction reaction, the equilibrium constant can be calculated because the equilibrium concentration of silver and the initial concentration of silver and Cyanex 302 are all known. The equilibrium constant calculated from Figure E1 by considering reaction stoichiometry of extraction reaction are 2.47, 1.16, and 0.118 for treat ratio 1:3, 1:5 and 1:7 respectively.

6.3 A Comparison of Model and Experimental Data

The validity of the proposed model was investigated with several experimental data such as the effect of carrier, stripping agent and surfactant concentrations, treat ratio, agitation speed and size of emulsion droplets. These results will show the model reliability for silver extraction from photographic wastes solution. In addition, if there is any small deviation between simulation results and experimental data, it will consider the possibility of random errors which are from instrument or manual behavior in experiments.

6.3.1 Effect of Carrier Concentration

The effect of carrier concentration on the silver extraction is displayed in Figure 6.2. The initial extraction performance increased with the increase in the carrier concentration. The figure shows that at carrier concentration 0.01 M, the simulated result of silver extraction performance is higher than experimental data. The reason is low viscosity of membrane which is referring to emulsion stability. Although the decrease on viscosity will increase the solute diffusivity in membrane phase, but in experiment, emulsion instability will diminish the extraction performance. However, the extraction performance drives to almost similar result at minutes 15. It is due to the trade-off of emulsion stability and diffusivity of complexes in membrane phase.

The result also shows that the extraction performance of 0.03 M and 0.05 M Cyanex 302 are quite similar to the prediction results within 10 minutes process. However, after 10 minutes process the experimental data shows a deviation from simulated results. It is a reason of emulsion instability for longer extraction time and the cause of swelling of emulsion globules. It is the fact that the water transfer from the external to the internal phases will concentrate the remaining metal content in the external phase. However, in this model the assumption was made of constant volume of the external phase during the process.

On the other hand, it is expected that a very high content of carrier in the membrane (more than 0.05 M) does not result in an increase in viscosity, which leads to larger globules (Teramoto *et al.*, 1983) but the increase in globule size will reduce the mass transfer area and lead to decrease in the extraction performance.

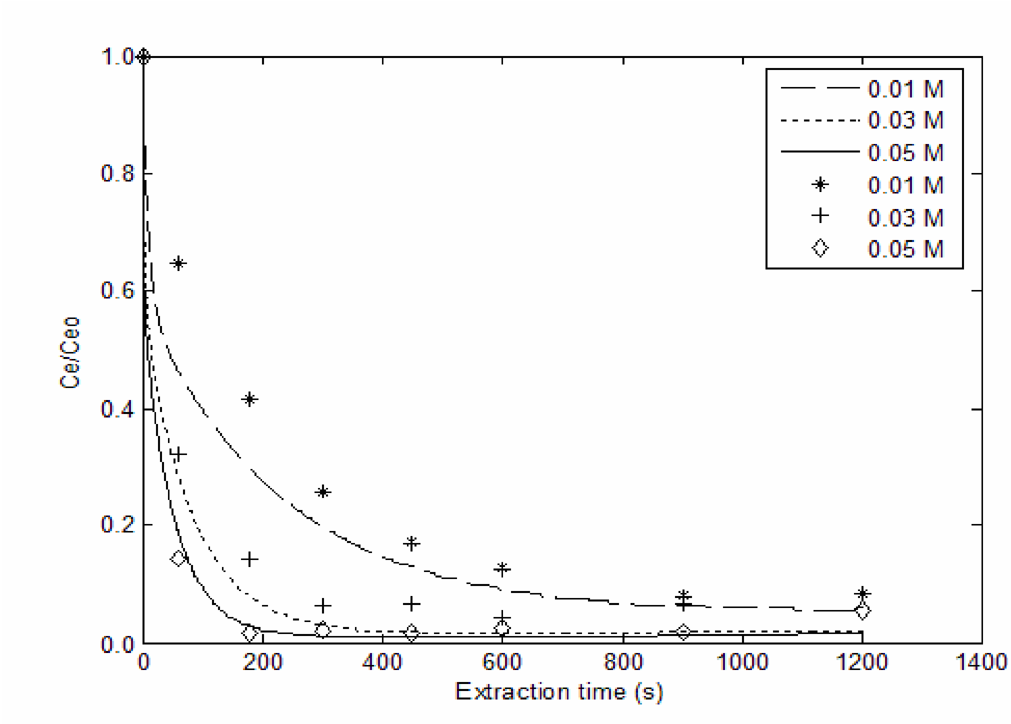


Figure 6.2: Effect of carrier concentration in the membrane phase (----, …., ___; simulation results. The other typical conditions are described in Table 6.1)

6.3.2 Effect of Treat Ratio (TR)

Figure 6.3 shows the comparison of simulation results and experimental data of varies treat ratio. The results show that, no satisfactory prediction is obtained for treat ratio 1:7. However, the model proved that the ELM system of silver is very economical at treat ratio 1:5. For TR less than 1:5, the degree of extraction performance was decreased experimentally. The results show that the deviation of simulation and experimental results is quite high especially after 3 minute process. Theoretically the extraction performance will increase when the extraction proceed. It is because in modeling, we are assuming that the emulsion break-up are constant and well mixed during the extraction process. In reality, from the experimental observation, no emulsion breakage occur initially but when the extraction proceed, the emulsion globules start to swell and broke down due to shear or hydrodynamic effect of the process.

On the other hand, the treat ratio also influence the stirring efficiency, because it is assumed the well mixed phenomena occur in the model whereas during the process practically the well mixing only in the bottom of the extractor. In this situation, no reliable prediction is obtained if the swelling and hydrodynamic effects of mixing are not included in the model.

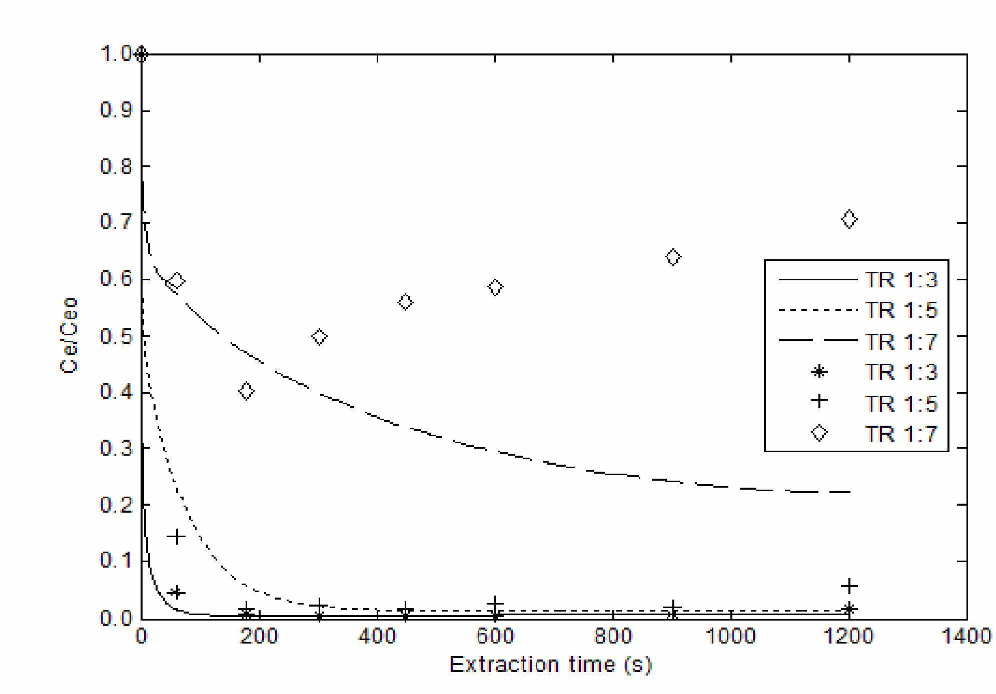


Figure 6.3: Effect of treat ratio on silver extraction (----, …., ___; simulation results. The other typical conditions are described in Table 6.1)

6.3.3 Effect of Stripping Agent Concentration

Figure 6.4 shows that the extraction of silver is enhanced with increasing the acidic thiourea concentration in the stripping phase. It is due to the difference of chemical potential of the external and the internal phases act as the main driving force between the two aqueous phases in the ELM process. Thus, the extraction rate increased with the increase in acidic thiourea concentration from 0.5 to 1.0 M because the capacity of the receiving phase increased. However, the simulation results proved that in excess of thiourea (1.5 M) in 1 M H_2SO_4 in stripping phase, the extraction performance almost in the same trend with the experimental data. It is because no more reaction occurred with an excess of thiourea. Therefore, the deviation of experimental data at the end of the extraction process happen because of thiourea itself will disturb the emulsion stability. It is due to the solubility of thiourea in organic phase and also due to emulsion swelling and the break-up phenomena during the extraction process. The difference between these two results also shows that the system is more concern toward emulsion swelling.

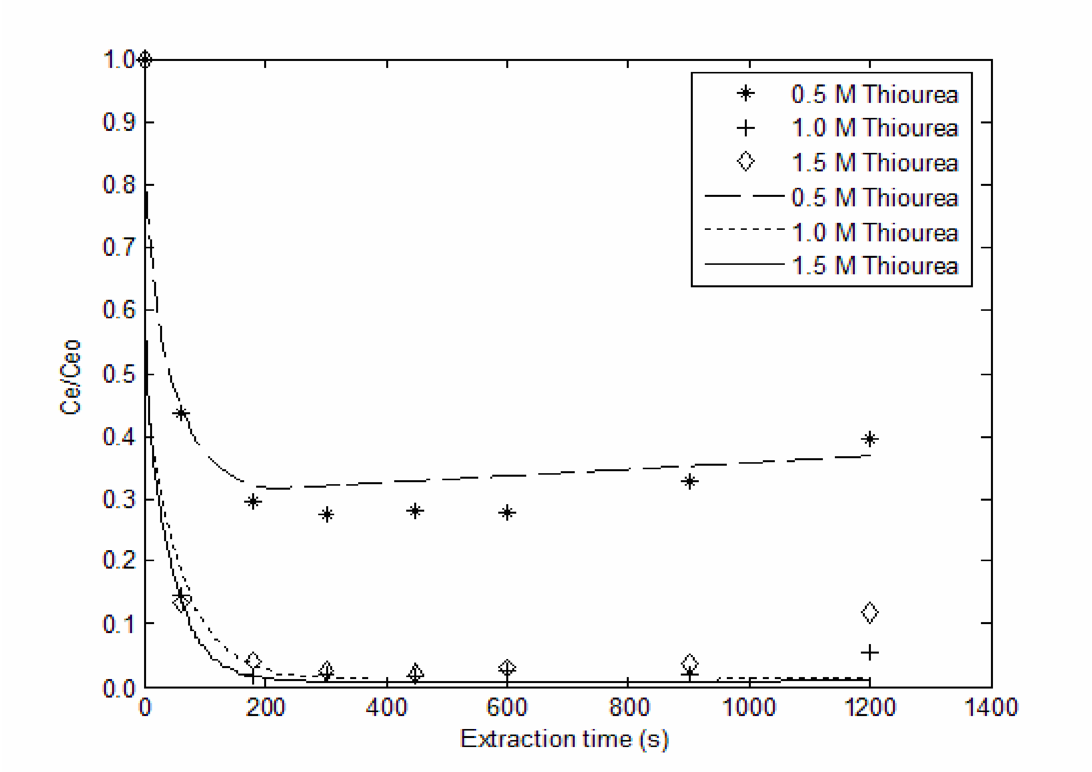


Figure 6.4: Effect of stripping solution concentration on silver extraction (----, …., ___; simulation results. The other typical conditions are described in Table 6.1)

6.3.4 Effect of Stirring Speed

Figure 6.5 illustrates the silver extraction rate at various speed of extraction. By increasing the level of agitation, the size of emulsion globules decreases. Theoretically the extraction performance will increase because of high interfacial area of reaction. As other authors have pointed out, the external surface area of globules rather than the internal phase droplet surface area controls the extraction process with ELMs (Ho and Sirkar, 1992, Rautenbach and Machhammer, 1988). However, in this system a large deviation was obtained between simulation results and experimental data for higher speed. It is due to a few reasons. The main reason is the size of emulsion globules. Thus, the water transfer is also promoted by increasing the stirring speed. As shown in Figure 6.5, the model deviated from the experimental data for speed 200 and 300 rpm. It is expected at higher speed which is above a critical value; increasing speed not only does not increase the extraction efficiency considerably, but also affects the stability of the emulsion and increase the swelling potential.

On the other hand, at lower speed rate, the extraction performance was less than the theoretical approximation. It is due to slow diffusion rate of solute to the external interface especially at initial process. However if the process was continue for longer extraction time it will promote more capacity of silver extracted from the external aqueous phase. It is estimated that the extraction will complete after certain time. Therefore, due to limitation in interface stability and requirement to minimize the run time for the experiment, moderate speed was required to obtained high extraction performance.

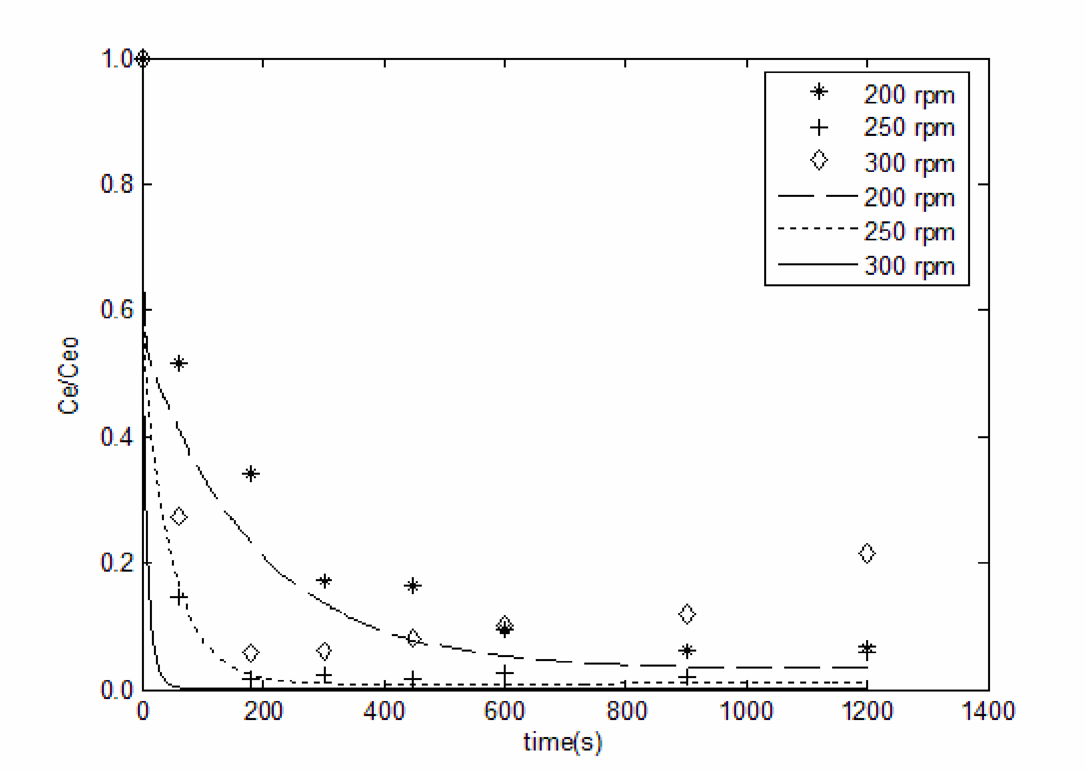


Figure 6.5: Effect of agitation speed on silver extraction (----, …., ___; simulation results. The other typical conditions are described in Table 6.1)

6.3.5 Effect of Surfactant Concentration

This model also tested for a different concentration of Span 80. It is known that the increase in the concentration of surfactant does not favour the kinetics of extraction (Marr *et al*., 1992). This is because of the increase in liquid membrane viscosity. Figure 6.6 shows that the simulation results demonstrate that there are satisfactory correlation with the experimental data for only 5 % (w/v) Span 80. However, the 1 and 3 % (w/v) of Span 80 the deviation occurred after 3 minutes running process. It is due to emulsion instability which cannot be predicted in the model developed. At lower surfactant concentration, the viscosity of the liquid membrane was decreased as shown in Table 5.4. As a result, the increase of diffusion coefficient and the mass transfer coefficient will increase the extraction performance theoretically. However, in this experimental work, only a little changes in liquid membrane viscosity is observed. On the other hand, the size of emulsion drops also influence by the amount of surfactant used in liquid membrane formulation. At high concentration of surfactant, the size of globules increased (Reis and Carvalho, 2004). Thus, these proved that the surfactant concentrations used in this study are in suitable range to generate good extraction performance.

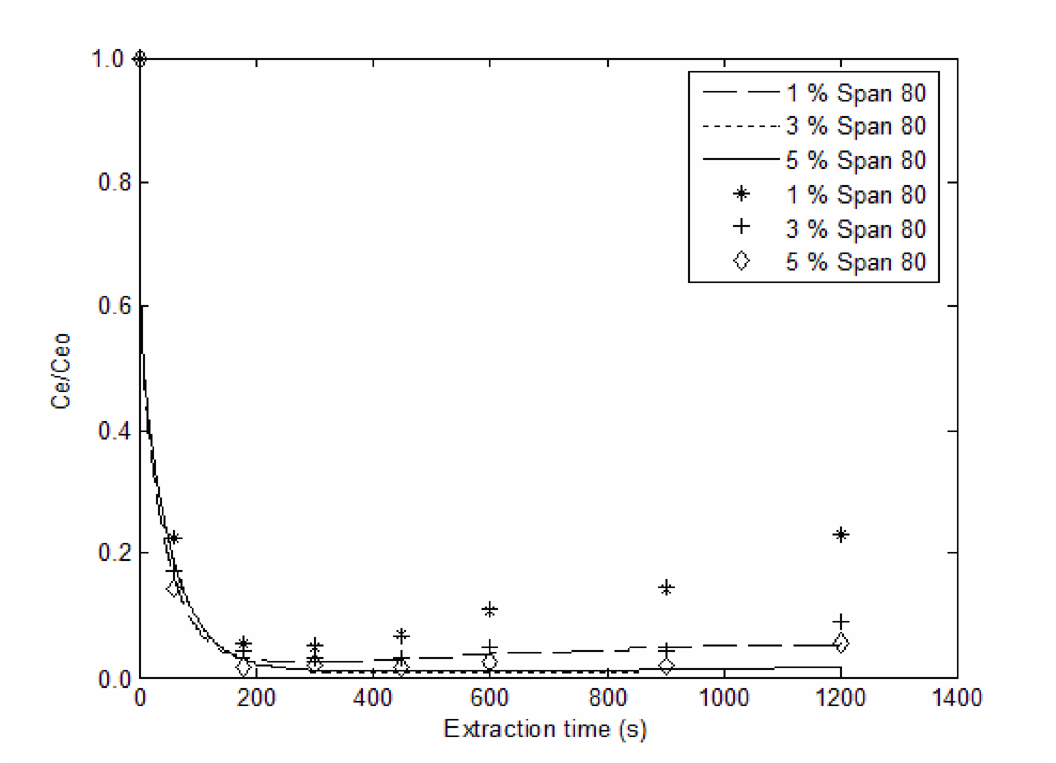


Figure 6.6: Effect of surfactant concentration in the membrane phase (----, …., ___; simulation results. The other typical conditions are described in Table 6.1)

6.3.6 Effect of Emulsion Droplets Size

The effect of homogenizer speed was also tested in this study. Figure 6.7 shows the simulation results and experimental data at different speed of homogenizer within 10 minutes extraction process. As reported in Chapter 5, the size of emulsion droplets depends on the speed of homogenizer. At high speed, smaller emulsion droplets were produced and the area of stripping reaction increased. Thus, the rate of reaction will increase gradually during the process. However, from experimental observation the extraction performances decrease after certain time due to the stability of emulsion. Therefore, the speed of homogenizer in emulsion making is very important in term of producing very small stable emulsion. It also important in determining the effective diffusivity in ELM system as illustrated in Equation 6.12. The smaller size of emulsion droplets will increase the values of effective diffusivity and this increase the extraction and recovery performance.

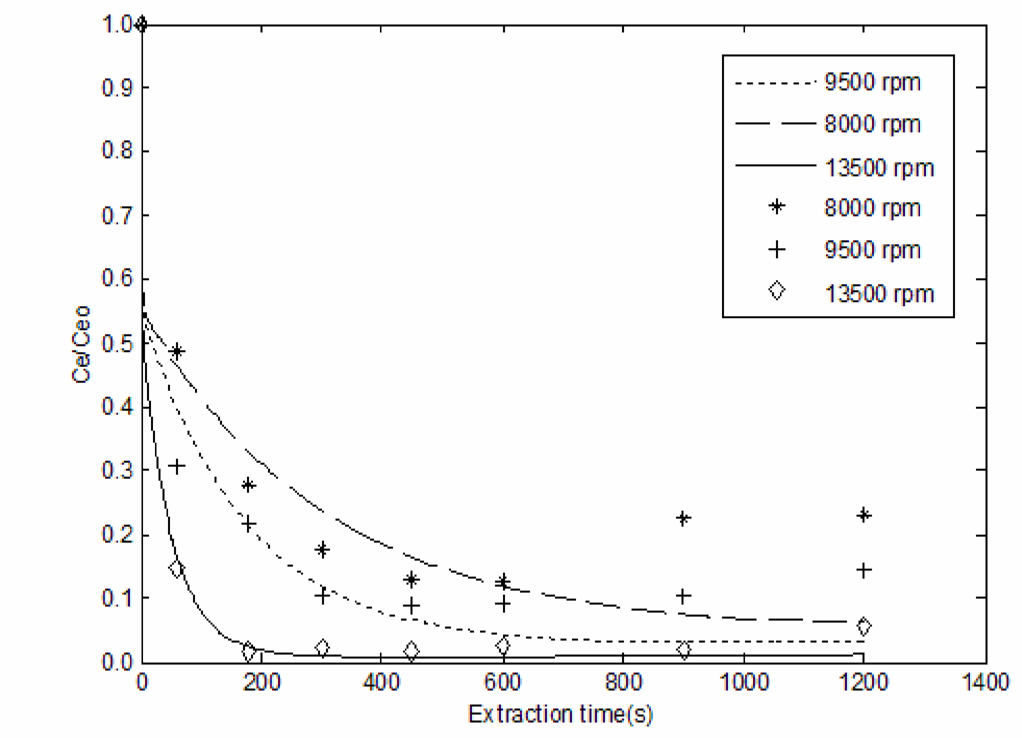


Figure 6.7: Effect of homogenizer speed on silver extraction (----, …., ___; simulation results. The other typical conditions are described in Table 6.1)

6.4 Summary

A dynamic ELM model including breakage of emulsion droplet was presented and solved numerically. The method of line was used to solve the model and a stable numerical procedure was found for practical ranges of application in silver extraction from liquid photographic wastes. Simulation shows that the simulation result was highly correlated to the experimental data especially at typical conditions. However, at some conditions the deviation of results occurred and a few concrete reasons were presented. In spite of all the approximation done in this work, the agreement between experimental and simulation results is quite good, mainly under moderate agitation speed and low extraction time up to 15 minutes.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The feasibility of ELM extraction of silver from real liquid photographic wastes was studied in this research. It was demonstrated that the ELM technique was very promising in extracting and recovering silver from photographic wastes.

In order to achieve the objectives, various carrier and strip agent were tested in determining the suitable liquid membrane component in ELM process. It was found that Cyanex 302 and acidic thiourea provide very attractive results as carrier and stripping agent to silver as a target metal ion. It also gives high selectivity to silver over the other metals. On the other hand, kerosene was chosen as an organic media for liquid membrane because it is less toxic and has low solubility in water and also provides high emulsion stability compared to toluene and n-dodecane systems. Beside, tetramethylthiuram disulfide in toluene also shows good capability in extracting silver. It provides good emulsion stability as Cyanex 302.

Since the key factor that influence the ELM process was the liquid membrane components, further investigation was carried out to study the effect of various concentrations of carrier, surfactant, and stripping agent, agitation speed and emulsion droplets size. The general conclusions of these effects are as follows:

i) The most suitable Cyanex 302 concentration is 0.03 M in kerosene which provided high extraction and recovery efficiency of silver in receiving phase.

Increasing the carrier concentration exceeding the critical value will cause liquid membrane contamination with unstripped metal-carrier complex during the ELM process. It is known that, ELM with carrier mediated mass transfer is a process where carriers act as a shuttle to carry solute from external phase into internal phase. Therefore, only a little concentration is needed to let this system running. However, appropriate concentration is needed to make shortest extraction time due to emulsion breakage and stability during the process.

ii) The ratio of emulsion to external phase volume can significantly affect the extraction efficiency. The incomplete extraction of silver from the external phase occurred if the treat ratio is less than 1:5 at presented formulation of internal phase reagent. The smallest treat ratio means that less amount of emulsion to extract silver into receiving phase while an increase treat ratio over certain limit will lead to swelling phenomena due to water transfer from external to internal phases. Therefore, a favorable treat ratio in this ELM system is 1:5.

iii) The internal phase extraction efficiency is the best with the 1.0 M thiourea in 1.0 M H_2SO_4 solution which gives high extraction and recovery performance. The decrease of silver extraction efficiency is caused by excess of thiourea or solution acidity. Therefore, no more thiourea is permitted in certain equivalent solution acidity and the other way of.

iv) The suitable surfactant used in liquid membrane component is 3% (w/v) Span 80 that provides good emulsion stability during the ELM process. The increase of surfactant concentration will affect the recovery efficiency. An excess of surfactant will lead to increase in thickness of resistance layer around the emulsion and this diminished the reaction and mass transfer of solute into receiving phase.

v) Size of emulsion globules plays an important role in ELM process. The adequate speed should be used to produce high mass transfer rate and at the same time emulsion breakage caused by shear and hydrodynamic effect must be avoided. Therefore the extractor must be designed properly including the size of extractor, impeller type and size and others consideration about motor stirrer and speed. In this study the most suitable speed is 250 rpm with magnetic stirrer.

vi) The size of emulsion droplet also plays an important factor in producing high stripping efficiency. The smallest size will provide high interfacial area of stripping efficiency. Therefore, 13500 rpm homogenizer speed in 5 minutes time should be used in emulsion preparation.

vii) The preliminary study of using tetramethylthiuram disulfide as a carrier show that it is also good in extracting silver from photographic waste solution in ELM process. However, it only dissolved in certain diluent especially in polar diluent therefore it is not recommended in ELM process in term of emulsion stability.

Furthermore, membrane breakage and swelling (apparent swelling) have also encountered during the ELM extraction process. The results show that many factors influencing this study such as concentrations of Span 80 and Cyanex 302, agitation speed and types of stripping agent used. It was found that from the experimental results, the breakage ratio of the emulsion is very small because the ratio of external phase concentration, C_e/C_{eo} curve with time does not oscillate very much except for longer extraction time. However, at certain condition the breakage was high such as at low treat ratio, system in excess acidity and thiourea concentration in internal phase, bigger size of emulsion droplets and also low concentration of surfactant.

In addition, the feasibility study of the prospect of ELM continuous process is also covered in this thesis. The result shows that this liquid membrane can be recycled but the efficiency of extraction decreased. Therefore, to maintain the extraction performance, this recycling liquid membrane should be mixed with fresh liquid membrane with certain ratio before homogenizing process. The proposed schematic diagram of the continuous process is shown in Figure 5.25. On the other hand, like the new emulsion liquid membrane process, this system is expected can easily be applied in industry. Because the extraction time of this system is very short, around 15 minutes, the height of the extraction tower for the scale-up plant should also be short.

The model of ELM silver extraction was established which considering mass balances in emulsion globules and the external phase. This model also took into account the leakage of membrane phase. The effective diffusivity D_{eff} , is based on membrane phase concentration and emulsion globules size. The instantaneous equilibrium for extraction reaction is considered on the surface of emulsion globules and local phase equilibrium which always exists for the whole emulsion globules due to the fast stripping reaction. This model was successfully solved numerically using MATLAB software. The model predictions match with the experimental data very closely especially at typical conditions. However, at certain parameters deviation of the model from the experimental data was observed. It is due to the assumptions and some experimental factors not considered in the model such as the moving boundary condition and swelling rate.

7.2 Recommendations and Future Works

This work stumbled upon a few interesting problems which can be subjected for future research. Therefore, further studies in a number of aspects related to the present investigation could be carried out to comprehend various issues.

i) The main issues in ELM application is emulsion stability. Although the stability of emulsion produced in this study is good enough to extract silver from photographic wastes, it cannot stand long extraction time. Therefore the use of surfactant that can stabilize and transport less water during the process should be used like polyamine surfactant instead of using Span 80.

ii) To avoid the agglomeration of emulsion droplets, a device to disperse the emulsion should be designed properly to enhance extraction efficiency. To produce well mixed emulsion globules during the extraction process, the use of magnetic stirrer for high volume treatment was not allowed. Therefore the extractor must be designed properly for well mixed process during the extraction time. The design should be also consider the type of impeller, size and it position.

iii) To elucidate more detail about swelling phenomena, the used of microscopic camera is required to measure the changes of emulsion globules size during the extraction process. Therefore, the rate of swelling can be determined correctly instead of measuring the emulsion volumes. To study the swelling caused by water transfer into W/O emulsion, Karl Fisher method can be used to measure the water content in liquid membrane during the extraction process.

iv) Emulsion breakage can be measured more accurately using tracer. This method can be carried out by putting a tracer in the internal phase and measuring the amount of tracer that appears in the external phase during the extraction process.

v) Demulsification process is a very important part in the final ELM process to recover solute (silver) in the receiving phase and liquid membrane recycling process. Therefore the use of high voltage demulsifier with high frequency (>800 Hz) was suggested to let emulsion break rapidly. Bailes and Larkai (1982) and Yan *et al*. (1990) found that under the constant voltage, a critical frequency existed was enhanced with increasing frequency. Moreover, high voltage was suggested but it must be noted that excessive high voltages should not be applied because the high voltage is liable to damage the insulating layer and thus cause sparking. Concerning this effect, Hsu and Li (1985) found that the insulation material having a dielectric constant above 4 offered better demulsification performance. Therefore, detail research should be made in order to design more sophisticated and reliable demulsifier to demulsify any emulsion system.

In order to develop this ELM system for industrial use, these studies have some beneficial advantages. There are the tendencies of silver recovery with high selectivity to silver and also the recycling of liquid membrane. As a result, the continuous process is very promising in extending to pilot scale study.

In addition for all listed conclusions and suggestions above, it is known that ELM is related much with emulsion stability. The effectiveness of ELM extraction of silver from photographic wastes depends more on this matter. In order to solve this problem the use of hollow fiber contactor (HFC) in ELM process was suggested. Hu (1997) shows that the use of hollow fiber contactors in copper extraction reduces swelling and leakage of liquid membrane and the stability of ELM are less crucial when combined with HFC. Therefore, it would be interesting to set-up this rig for future studies.

REFERENCES

Abou-Nemeh, I. and Van Peteghem, A.P. (1993). Membrane Recycling in the Surfactant Membrane Process. *Ind. Eng. Chem. Res*. 32:1431-1437.

Akretche, D-E., Gherrou, A., and Kerdjoudj, H. (1997). Electrodialysis of Solutions Obtained by Elution of Cyanide Complexes from Anionic Exchange Resin by Means of Acidic Thiourea. *Hydrometallurgy*. 46: 287-301

Alam, M. S., Inoue, K., Yoshizuka, K., Dong, Y., and Zhang, P. (1997). Solvent Extraction of Silver from Chloride Media With Some Commercial Sulfur-Containing Extractants. *Hydrometallurgy*. 44(1-2): 245-254.

Alguacil F. J., Coedo A. G., and Dorado M. T. (2000), Transport of chromium(VI) through a Cyanex 923-xylene flat-sheet supported liquid membrane, *Hydrometallurgy*. 57: 51-56.

Alguacil, F. J. (1999). Solvent Extraction of Indium (III) by LIX 973N. *Hydrometallurgy*. 51: 97-102.

Alguacil, F. J., Cobo, A., and Alonso, M. (2002). Copper Separation from Nitrate/Nitric Acid Media Using Acorga M5640 Extractant. Part I: Solvent extraction Study. *Chem. Eng. J*. 85: 259-263.

Almela, A. and Elizalde, M.P. (1995). Solvent Extraction of Cadmium(II) from Acidic Media by Cyanex 302. *Hydrometallurgy*. 37: 47-57.

Alonso, A. I. and Pantelides, C. C. (1996). Modelling and Simulation of Integrated Membrane Processes for Recovery of Cr(VI) with Aliquat 336. *J. Membr. Sci.* 110: 151-167.

Alonso, A.I., Urtiaga, A. M., Zamacona, S., and Ortiz, I. I. (1997). Kinetic Modeling of Cadmium Removal from Phosphoric Acid by Non-dispersive Solvent Extraction. *J. Membr. Sci*. 130: 193-203.

Babcock, W.C., Friesen, D. T., and Lachapelle, E.D. (1986). Liquid Membranes for Separating Uranium from Vanadium and Uranium from Molybdenum. *J. Membr. Sci*. 26(3): 303-312.

Babcock, W.C., Baker, R.W., Lachapelle, E.D., and Smith, K.L. (1980). The mechanism of uranium transport with a tertiary amine. *J. Membr. Sci.* 7(1): 71-87.

Bailes, P.J. and Larkai, S.K.L. (1981). An Experimental Investigation into the use of High Voltage D.C. Fields for Liquid Phase Separation. *Trans. I. Chem. E.* 59(4): 229-237.

Bailes, P.J. and Larkai, S.K.L. (1982). Liquid Phase Separation in Pulsed DC Fields. *Trans. I. Chem. E.* 60: 115-121.

Bailey, T. and Mahi, P. (1987). The Effect of Diluents on The Metal Extracted and Phase Separation in the Extraction of Aluminium With Mononony1 Phosphoric Acid. *Hydrometallurgy.* 18: 351-365.

Baird, I.H.M. and Hanson, C. (1983). *Handbook of Solvent Extraction*. New York: John Wiley and Sons.

Bart, H. J., Jungling, H., Ramaseder, N., and Marr, R. (1995). Water and Solute Solubilization and Transport in Emulsion Liquid Membranes. *J. Membr. Sci.* 102: 103-112.

Baumann, W. and Grafen, M. (2001). *Emission Scenario Document Photographic Industry IC-10*. Institute for Environmental Research University Dortmund (INFU).

Becher, P. (1985). (Ed.). *Encyclopedia of Emulsion Technology*. New York: Marcel Dekker.

Benavente, J. and Jonsson, G. (2000). Electro Kinetic Characterization of Composite Membranes: Estimation of Different Electrical Contributions in Pressure Induced Potential Measured Across Reverse Osmosis Membrane. *J. Membr. Sci*. 172: 189-197.

Bhavani, R., Neena, T., and John, W. (1994). Emulsion Liquid Membranes for Wastewater Treatment: Equilibrium Models for Some Typical Metal-extractant Systems. *Environ. Sci. Technol*. 28: 1090-1098.

Bhowal, A. and Datta, S. (2001). Studies on Transport Mechanism of Cr(VI) Extraction from Acidic Solution Using LSM. *J. Membr. Sci*. 188: 1-8.

Brooks, C.S. (1991). *Metal Recovery from Industrial Waste*. Michigan: Lewis Publishers Inc.

Bunge, A.L. and Noble, R.D. (1984). A Diffusion Model for Reversible Consumption in Emulsion Liquid Membrane. *J. Membr. Sci*. 21: 55-71.

Byers, C.H. and Amarnath, A. (1995). Understand the Potential of Electro-Separations. *Chem. Eng. Progress*. 2: 63-69.

Cahn, R. P., Frankenfeld, J. W., Norman, N. Li, Naden, D., and Subramanian, K. N. (1981). Extraction of Copper By Liquid Membranes. In: Norman N. Li. ed. *Recent Developments in Separation Science*. Volume VI. Boca Raton, Florida: CRC Press, Inc. 51-64.

Caravaca, C., Alquacil, F. J., Sastre, A., and Martinez, M. (1996). Extraction of Gold(I) Cyanide by the Primary Amine Tridecylamine. *Hydrometallurgy*. 40: 89-97.

Chapman, T. W. (1987). Extraction-Metals Processing. In: Rousseau, R. W. ed. *Handbook of Separation Process Technology*. United States of America: John Wiley & Sons, Inc.

Chakraborty, R. and Datta, S. (1994). Transport of Te^{4+} Through Liquid Surfactant Membrane Using D2EHPA as the Carrier. *J. Membr. Sci*. 96: 233-240.

Chaudry, M.A., Ul-Islam, N., and Ahmad I. (1994). Extaction and Stripping Study of Strontium Ions Across D2EHPA-TBP-Kerosene Oil Based Supported Liquid Membranes. *J. Radioanal. Nucl. Chem*. 185(2): 369.

Chaudry, M.A., Ul-Islam, N., Ur-Rehman, N., and Yasin Z. (1995). Nitrate Ion Transport Across TBP-Kerosene Oil Supported Liquid Membranes Coupled With Uranyl Ions. *J. Radioanal. Nucl. Chem*. 189(2): 207.

Chiarizia, R. (1991). Application of Supported Liquid Membranes for Removal of Nitrate, Technetium(VII) and Chromium(VI) from Groundwater. *J. Membr. Sci*. 55: 65-77.

Chiarizia, R., Horwitz, E. P., Rickert, P.G., and Hodgson, K. M. (1990). Application of Supported Liquid Membranes for Removal of Uranium from Groundwater. *Sep. Sci. Technol*. 25(13-15): 1571-1586.

Chitra, K. R., Gaikwad, A. G., Surender, G. D., and Damodaran, A. D. (1997). Studies on Ion Transport of Some Rare Earth Elements Through Solvating Extractants Immobilized on Supported Liquid Membranes. *J. Membr. Sci*. 125: 257-268.

Chormann, F. H., Mary, Jo Spencer Jr. , Berry Lyons Wm., and Mayewski, P. A. (1985), A Solvent Extraction Technique for Determining Concentrations of Gold and Silver in Natural Waters**.** *Chemical Geology*. 53(1-2): 25-30.

Clifford, A. H. and Gessner G. H. (1976). *Glossary of Chemical Trems*. New York: Van Nostrand Reinhold Company.

Coelhoso, I. M., Crespo, J.P.S.G., and Carrondo, M.J.T. (1997). Kinetics of Liquid Membrane Extraction in Systems with Variable Distribution Coefficient. *J. Membr. Sci*. 127: 141-152.

Coelhoso, I. M., Moura, T. F., Crespo J.P.S.G., and Carrondo, M.J.T. (1995). Transport Mechanisms in Liquid Membranes with Ion Exchange Carriers. *J. Membr. Sci*. 108: 231-244.

Colinart, P., Delepine, S., Trouve, G., and Renon, H. (1984). Water Transfer in Emulsified Liquid Membrane Processes. *J. Membr. Sci*. 20: 167-187.

Cook, F.L. and Szmokaluk, V. (1971). Proceeding International Solvent Extraction Conference. The Hague: Pub. Soc. Chem. Ind.: 145-151.

Cooley, A. and Vacco, D. (1993). Factors Limiting the Recovery, Regeneration and Reuse of Photographic Processing Solution. *J. Imag. Sci. Technol*. 37(6): 603-606.

Cote, G. and Bauer, D. (1980). Liquid-Liquid Extraction of Germanium with Oxine Derivatives. *Hydrometallurgy*. 5: 149-160.

Cox, F. A. and Bhatnagar, A. (1990). Analytical Utility of Coupled Transport Across a Supported Liquid Membrane; Selective Preconcentration of Zinc. *Talanta.* 37(11): 1037-1041.

Dalton, H.E. and Price, M.G. (1982). *Science Technology of Tributyl Phosphate*. Vol. 3. Boca Reton: CRC Press.

Daneisi, P.R., Horwitz, E.P., and Vandergrift, G.F. (1981). Mass Transfer Rate Through Liquid Membranes: Interfacial Chemical Reactions and Diffusion as Simultaneous Permeability Controlling Factors. *Sep. Sci. Technol*. 16: 201-211.

Deparment of Environment, Health, and Natural Resources (DEHNR) (2001). *Silver Recovery Systems and Waste Reduction in Photoprocessing*. North Carolina Division of Pollution and Environmental Assistance: Waste Reduction Fact Sheet.

Ding, X.C. and Xie, F.Q. (1991). Study of the Swelling Phenomena of Liquid Surfactant Membrane. *J. Membr. Sci*. 59: 183-188.

Douglas, Way, J., Richard, D. N., Thomas, M. F., and Dendy, S. E. (1982). Liquid Membrane Transport: A Survey. *J. Membr. Sci*. 12: 239-259.

Draxler, J. and Marr, R. (1986). Emulsion Liquid Membranes. Part I : Phenomenon and Industrial Application. *Chem. Eng. Process*. 20: 319-329.

Dreher, T. M., Glass, J., O'Connor, A. J., and Stevens, G. W. (1999). Effect of Rheology on Coalescence Rates and Emulsion Stability. *AIChE J*. 45: 1182-1190.

Frankenfeld, J.W., Asher, W.J., and Li N.N. (1978). *Recent Developments in Separation Science*; N.N. Li, Ed. Chemical Rubber Co. 4: 39-52.

Frankenfeld, J.W., Chan, R.P., and Li, N.N. (1981). Extraction of copper by liquid membranes. *Sep. Sci. Technol*. 16(4): 385-402.

Freiser, H. (1973). Solvent Extraction. In. Karger, B. L., Synder, L. R., and Horvath, C. ed. *An Introduction to Separation Science*. Canada: John Wiley & Sons, Inc.

Friesen, D. T., Babcock, W. C., Brose, D. J., and. Chambers, A. R. (1991). Recovery of citric acid from fermentation beer using supported-liquid membranes. *J. Membr. Sci*. 56(2): 127-141

Fu, J., Nakamura, S., and Akiba, K. (1995). Extraction of Platinum(IV) with Trioctylamine and its Application to Liquid Membrane Transport. *Sep. Sci. Technol*. 30(4): 609-617.

Gabriel, S., and Abraham, M. (1999). Cadmium Removal from Aqueous Solutions by a Emulsion Liquid Membrane- The Effect of Resistance to Mass Transfer at the Outer Oil-Water Interface. *Colloids Surf. A: Physicochemical and Engineering Aspects*. 151: 77-83.

Garti, N., Magdassi, S., and Whitehill, D. (1985). Transfer Phenomena Across the Oil Phase in Water-Oil-Water Multiple Emulsions Evaluated by Coulter-Counter. *J. Coll. Interf. Sci*. 104: 587-595.

Geankoplis, C. J. (1993). *Transport Processes and Unit Operation*. 3rd ed. New Jersey: Prentice Hall International Inc. 399-402.

Gherrou, A. and Kerdjoudj, H. (2002). Removal of Gold as $Au(Tu)_2^+$ complex with a Supported Liquid Membrane Containing Macrocyclic Polyethers Ligands as Carriers. *Desalination*. 144: 231-236.

Goddard, J. D. (1977). Further Application of Carrier-Mediated Transport Theory – A survey. *Chem. Eng. Sci*. 32: 795-809.

Goshima, T., Hori, K., and Yamamoto, A. (1994). Recovery of Silver from Radiographic Fixer. *Oral Surgery Oral Medicine Pathology*. 77: 684-688.

Goto, M., Kondo, K., and Nakashio, F. (1989a). Acceleration Effect of Anionic Surfactants on Extraction Rate of Copper with Liquid Surfactant Membrane Containing LIX65N and Nonionic Surfactant. *J. Chem. Eng. Jpn*. 22: 79-98.

Goto, M., Kondo, K., and Nakashio, F. (1989b). Extraction Kinetic of Copper with Liquid Surfactant Membrane Containing LIX65N and Nonionic Surfactant. *J. Chem. Eng. Jpn*. 22: 71-78.

Goto, M., Yamamoto, H., Kondo K., and Nakashio F. (1991). Effect of New Surfactant on Zinc Extraction with Liquid Surfactant Membranes. *J. Membr. Sci*. 57: 161-174.

Gu, Z., Winston, Ho, W.S., and Li, N.N. (1992). Design Consideration. In: Winston Ho W.S., Sirkar K.K. (Eds.), *Membrane Handbook*. Chapman Hall, New York. 656-700.

Guha, A. K., Yun, C. H., Basu, R., and Sirkar, K. K. (1994). Heavy Metal Removal and Recovery by Contained Liquid Membrane Permeator. *AIChE J*. 40(7): 1223-1237.

Halwachs, W. and Schugerl, R. (1980). The Liquid Membrane Technique –A Promising Extraction Process. *Int. Chem. Eng*. 20: 519-528.

Hanna, G.J. and Larson K.M. (1985). Influence of Preparation Parameters on Internal Droplet Size Distribution of Emulsion Liquid Membrane. *Ind. Eng. Chem. Res. Dev*. 24: 269-274.

Hanson, C. (1971). *Recent Advances in Liquid-Liquid Extraction*. Oxford, England: Pergamon Press.

Harpur, I.G., Wayth, N.J., Thew, M.T., Williams, T.J., and Urdahl, O. (1997). Destabilisation of Water-in-Oil Emulsions under the Influence of an A.C. Electric Field: Experimental Assessment of Performance. *J. Electrostatic*. 40&41: 135-140.

Hayworth, H.C., Ho, W.S., Burns Jr., W.A., and Li, N.N. (1983). Extraction of Uranium from Wet Process Phosphoric Acid by Liquid Membranes. *Sep. Sci. Technol*. 18(6): 493-521.

Heikki, L. (1999). *Removal of Harmful Metals from Metal Plating Wastewaters Using Selective Ion Exchangers*. University of Helsinki: Academic dissertation.

Hirato, T., Koyama, K., Awakura, Y., and Majima, H. (1990). Concentration of Mo(VI) from Aqueous Sulfuric Acid Solution by an Emulsion Type Liquid Membrane Process. *Material Transactions. JIM*. 31(3): 213-218.

Ho, W. S., Hatton, T. A., Lightfoot, E. N., and Li, N. N. (1982). Batch Extraction with Liquid Surfactant Membranes: A diffusion controlled model. *AIChE J*. 28(4): 662-670.

Ho, W.S. and Li, N.N. (1992). Theory. In: Ho, W.S. and Sirkar, K.K. eds. *Membrane Handbook*. New York: Van Nostrand Reinhold. 611-655.

Hochhauser, A. M. and Cussler, E. L. (1975). Concentrating Chromium with Liquid Surfactant Membranes. *AIChE Symp. Ser*. 71(152): 136-142.

Hong, P.O. and Lee, J.M. (1983). Unsteady-State Liquid-Liquid Dispersions in Agitated Vessels. *Ind. Eng. Chem.*, Process Design and Development. 22: 130-135.

Hong, P.O. and Lee, J.M. (1985). Changes of the Average Drop Sizes During the Initial Period of Liquid-Liquid Dispersions in Agitated Vessels. *Ind. Eng. Chem.* Process Design and Development. 24: 868-872.

Hou, W. and Papadopoulos K.D. (1996). Stability of Water-in-Oil-in-Water Type Globules. *Chem. Eng. Sci*. 51(22): 5043-5051.

Hou,W. Q. and Papadopoulos, K. D. (1996). Stability of Water-In-Oil-In-Water Type Globules. *Chem. Eng. Sci.* 51(22): 5043-5051.

Hu, S-Y. B. and Wiencek, J. M. (1998). Emulsion Liquid Membrane Extraction of Copper Using a Hollow Fiber Contactor. *AIChE J*. 44(3): 570-581.

Hubicki, Z. and Hubicka, H. (1995). Studies of Extraction of Removal Of Silver (I) from Nitrate Solutions by Cyanex 471X. *Hydrometallurgy*. 37: 209-219.

Hsu, E.C. and Li, N.N. (1985). Membrane Recovery in Liquid Membrane Separation Processes. *Sep. Sci. Technol*. 20(2-3):115-130.

Ibrahim, M.Y., Mostafa, R., Fahmy, M.F.M., and Hafez, A.I. (2001). Utilization of Electroflotation in Remediation of Oily Wastewater. *Sep. Sci. Technol.* 36: 3749-3762.

Inci, E., Rahmi, K., and Gungor, G. (1993). Extraction of Strontium Ions with Emulsion Liquid Membrane Technique. *J. Membr. Sci*. 80: 319-325.

Inoue, K., Baba, Y., Oka, T., Takagi, M., and Dohtsu, K. (1987). A Solvent Extraction Study of Silver(I), Palladium(II) and Mercury(II) with 2-tert-dodecylthiopyridine. *Hydrometallurgy*. 18: 265-272.

Irving, H.M.N.H. (1977). *Dithizone in Analytical Science Monographs*. London: The Chemical Society.

Itoh, H., Thein, M.P., Hatton, T.A., Wang, D.I.C. (1990). A Liquid Emulsion Membrane Process for the Separation of Amino Acid. *Biotech. and Bioeng*. 35: 853-860.

Itoh, H., Thein, M.P., Hatton, T.A., and Wang, D.I.C. (1990). Water Transport Mechanism in Liquid Membrane Process for the Separation of Amino Acids. *J. Membr. Sci.* 51: 309-322.

IUPAC (1993). Nomerature for Liquid-Liquid Distribution (solvent extraction). *Pure and Appl. Chem.* 65(11): 2373-2396.

Ivanov, I.B. and Kralchevsky, P.A. (1997). Stability of Emulsion Under Equilibrium and Dynamic Conditions. *Colloids Surf.* 128: 155-175.

Izatt, R. M., Lindh, G. C., Bruening, R. L. Peter, H., McDaniel, C. W., Bradshaw, J. S., and Christensen, J. J. (1988). Separation of Silver from Other Metal Cations Using Pyridine and Triazole Macrocycles in Liquid Membrane Systems. *Analy. Chem.* 60: 1694-1699.

Jean-Bernard Regnouf-de-Vains, Jean-Olivier Dalbavic, Roger Larnartine, Fenet B. (2001). Quantitative Solvent Extraction from Neutral Aqueous Nitrate Media of Silver(I) against Lead(II) with a New Calyx[4]arene-based Bipyridine Podand. *Tetrahedron Letters*. 42: 2681-2684.

Jiang, Y., Wang, F., Kim, D.H., and Lim, M.S. (2001). Modeling of the Permeation Swelling of Emulsion During Lactic Acid Extraction by Liquid Surfactant Membranes. *J. Membr. Sci*. 191: 215-223.

Johnson, B.M., Baker, R.W., Matson, S.L., Smith, K.L., Roman, I.C., Tuttle, M.E., and Lonsdale, H.K. (1987). Liquid Membranes for the Production of Oxygen-Enriched Air: II. Facilitated-Transport Membranes. *J. Membr. Sci*. 31(1): 31-67.

Juang, R. (1993). Modelling of the Competitive Permeation of Cobalt and Nickel in a di(2-ethylhexyl)phosphoric Acid Supported Liquid Membrane Process. *J. Membr. Sci*. 85: 157-166.

Kakoi, T., Goto, M., Kondo, K. and Nakashio, F. (1993). Extraction of Palladium by Liquid Surfactant Membranes using New Surfactants. *J. Membr. Sci*. 84: 249-258.

Kakoi, T., Horinouchi, N., Goto, M., and Nakashio, F. (1996). Selective Recovery of Palladium from a Simulated Industrial Waste Water by Liquid Surfactant Membrane Process. *J. Membr. Sci*. 118: 63-71.

Kakoi, T., Nishiyori, T., Oshima, T., Kubota, F., Goto, M., Shinkai, S., and Nakashio, F. (1997). Extraction of Rare Earth Metals by Liquid Surfactant Membranes Containing a Novel Cyclic Carrier. *J. Membr. Sci*. 136: 261-271.

Kalachev, A. A., Kardivarenko, L. M., Plate, N. A., and Bagreev, V. V. (1992). Facilitated Diffusion in Immobilized Liquid Membranes: Experimental Verification of the 'jumping' Mechanism and Percolation Threshold in Membrane Transport. *J. Membr. Sci*. 75: 1-5.

Kanungo, S. B. and Mohapatra, R. (1995). Coupled transport of Zn(II) Through a Supported Liquid Membrane Containing Bis(2,4,4-trimethylpantyl) Phosphinic Acid in Kerosene, I. A Model for Therate Process Involving Binary and Ternary Complex Species. *J. Membr. Sci*. 105: 217-226.

Kargari, A., Kaghazchi, T., and Soleimani, M. (2003). Role of Emulsifier in the Extraction of Gold (III) Ions from Aqueous Solutions Using the Emulsion Liquid Membrane Technique. *Desalination.* 162 (2004): 237-247.

Kasaini, H., Nakashio, F., and Goto M. (1998). Application of Emulsion Liquid Membranes to Recover Cobalt ions from a Dual-Component Sulphate Solution Containing Nickel Ions. *J. Membr. Sci*. 146: 159-168.

Kataoka, T., Nishiki, T., Kimura, S., and Tomioka, Y. (1989). Batch Permeation of Metal Ions Using Liquid Surfactant Membranes. *J. Membr. Sci*. 46: 67-80.

Kataoka, T., Nishiki, T., Yamauchi, M., and Zhong, Y. (1987). A Simulation for Liquid Surfactant Membrane Permeation in a Continuous Counter-Current Column. *J. Chem. Eng. Jpn*. 20(4): 410-415.

Keller, K. (1993). *Science and Technology of Photography*. New York: VCH Publisher.

Kiani, A., Bhave, R. R., and Sirkar, K. K. (1984). Solvent Extraction with Immobilized Interfaces in a Microporous Hydrophobic Membrane. *J. Membr. Sci*. 20: 125-145.

Kim, B., Moon, J.H., Yang, S., and Kim, J. (2002). Demulsification of Water-in-Crude oil Emulsions by a Continuous Electrostatic Dehydrator. *Sep. Sci. Technol*. 37: 1307-1320.

Kim, D. H., Wainwright, M. S., Chang, K. S., and Ma, G. (1996). Analytical and Numerical Solution of Fixed and Moving Boundary Problems for Liquid Surfactant Membrane Processes. *Chem. Eng. Sci*. 51(11): 3059-3064.

Kim, K., Choi, S., and Ihm, S. (1983). Simulation of Phenol Removal from Waste Water by Liquid Membrane Emulsion. *I&EC Fund*. 22: 167-172.

Kim, S-G, Lee, H-Y., Oh, J-K., and Lee, E-C. (1995). Stoichiometric Relation for the Extraction of the Gold-Thiourea Complex with D2EHPA. *Hydrometallurgy*. 38: 7-13.

Kim, S.J., Kim, S.C., and Kawasaki, J. (1997). Separation of Hydrocarbons by Liquid Surfactant Membrane with a Batch Stirred Vessel. *Sep. Sci. Technol*. 32: 1209-1221.

Kimura, K. and Shono, T. (1987). Liquid-liquid Extraction of Silver Ion with Benzothiacrown ether Derivatives. *Anal. Chim. Acta*. 194: 293-298.

Kimura, S. G., Matson, S.L., and Ward, W. J. (1979). Industrial Application of Facilitated Transport, In: Li, N. N. (Ed). *Recent Development in Separation Science*. Vol.5. Cleveland, Ohio: CRC Press.

Kinugasa, T., Watanabe, K., and Takeuchi H. (1989). Effect of Organic Solvents on Stability of Liquid Surfactant Membranes. *J. Chem. Eng. Jpn*. 22: 593-597.

Kojima, T., Nakayama, C., and Uemiya, S. (1994). Analysis of the Mechanism of Rare Earth Metal Permeation Through a Liquid Membrane with a Chelating Agent in the Feed Phase. *Can. J. Chem. Eng*. 72: 72--77.

Kondo, K., Kita, K., Koida, I., Irie, J., and Nakashio, F. (1979). Extraction of Copper with Liquid Surfactant Membranes Containing Benzoylacetone. *J. Chem. Eng. Jpn*. 12(3): 203-209.

Kondo, K., Yamamoto, Y., and Matsumoto, M. (1997). Separation of Indium(III) and Gallium(III) by Supported Liquid Membrane Containing Diisostearylphosphoric acid as a Carrier. *J. Membr. Sci*. 137: 9-15.

Kopp, A. G., Marr, R. J., and Moser, F. E. (1978). A New Concept for Mass Transfer in Liquid Surfactant Membranes without Carriers and with Carriers That Pump, *Inter. Chem. Eng. Symp. Ser*. 54: 279.

Kopunec, R. and Manh, T. N. (1992). Carrier-Medieted Transport of Rare Earth Elements Through Liquid Membranes; IV. Transport of Sc, Y, Ce, Eu, Gd, Tm, Yb Through a Supported Liquid Membrane Containing TBP. *J. Radioanal. Nucl. Chem*. 163(1): 131-144.

Kopunec, R. and Manh, T. N. (1993). Carrier-Medieted Transport of Rare Earth Elements Through Liquid Membranes; III. Transport of Sc, Y, Ce, Eu, Gd, Tm, Yb Through a Supported Liquid Membrane Containing DEHPA. *J. Radioanal. Nucl. Chem*. 170(1): 51-66.

Koval, C.A., Noble, R.D., Way, J.D., Louie, B., Reyes, A., Horn, G., and Reed, D. (1985). Selective Transport of Gaseous CO Through Liquid Membrane Using an Iron(III) Macrocycle Complex. *Inorganic Chem*. 24: 1147-1152.

Kremesec, V. J. (1981). Modelling of Dispersed Emulsion Separation Systems. *Sep. Purif. Methods.* 10: 117-157.

Kremesec, V. J. and Slattery, J. C. (1982). Analysis of Batch Dispersed-Emulsion Separation Systems. *AIChE J*. 28: 492-500.

Kubota, F., Goto, M., Nakashio, F., and Hano, T. (1995). Extraction Kinetics of Rare Earth Metals with 2-ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester Using a Hollow Fiber Membrane Extractor. *Sep. Sci. Technol*. 30(5): 777-792.

Kulkarni, P. S. (2003). Recovery of Uranium(VI) from Acidic Wastes Using Tri-n-octylphosphine Oxide and Sodium Carbonate Based Liquid Membrane. *Chem. Eng. J*. 92: 209-214.

Kulkarni, P.S., and Mahajani, V.V. (2002). Application of ELM Process for Enrichment of Molybdenum from Aqueous Solutions. *J. Membr. Sci*. 201: 123-135.

Kulkarni, P.S., Tiwari, K.K., and Mahajani, V.V. (2000). Membrane Stability and Enrichment of Nickel in Liquid Emulsion Membrane Process. *J. Chem. Technol. Biotechnol*. 75(7): 553-560.

Kumar, M., Sharma nee Bhalla, V., and Babu, J. N. (2003). Synthesis and Binding Studies of New bis-calix[4]arene Aromatic and Heteroaromatic Units. *Tetrahedron.* 59: 3267-3273.

Kuo, Y. and Gregor, H. P. (1983). Acetic Acid Extraction by Solvent Membrane. *Sep. Sci. Technol*. 18(15): 421-440.

Lacey, D.G. (1972). *Ion Exchange and Solvent Extraction of Metals*. Chinester: Wiley-Interscience.

Lacey, R.E. (1972). Membrane Separation Processes. *Chem. Eng*. 56-74

Lachowicz, E., Rozanska, B., Teixidor, F., Meliani, H., Barboiu, M., and Hovnanian, N. (2002). Comparison of Sulphur and Sulphur-Oxygen Ligands as Ionphores for Liquid-Liquid Extraction and Facilitated Transport of Silver and Palladium. *J. Membr. Sci*. 210: 279-290.

Lang, S.B. and Wilkie, C.R. (1971). A Hydrodynamic Mechanism for the Coalescence of the Liquid Drops: I. Theory of Coalescence at a Planar Interface. *Ind. Eng. Chem. Fundam.* 10: 329.

Lee, J-M. and Lim, K-H. (2004). Changes in Morphology of Three-phase Emulsions with Temperature in Ternary Amphiphile/Oil/Water Systems. *Colloids Surf. A: Physicochem. Engng. Aspects*. 248(1-3): 57-65

Lee, K-H., Evans, D.F., and Cussler, E.L. (1978). Selective Copper Recovery with two Types of Liquid Membranes. *AIChE J.* 24: 860-868.

Lee, S. C., Ahn, B. S., and Lee, W.K. (1996). Mathematical Modeling of Silver Extraction by an Emulsion Liquid Membrane Process. *J. Membr. Sci*. 114: 171-185.

Lee, S.C., Lee, K.H., Hyun, G.H., and Lee, W.K. (1997). Continuous Extraction of Penicilin G by an Emulsion Liquid Membrane in a Countercurrent Extraction Column. *J. Membr. Sci*. 124: 43-51.

Lewis, R.G. (1990). Process of Extraction of Gallium from Aqueous Solutions Thereof. US Patent 4,965,054, Oct 23.

Li, N. N., US Pat. 3410794 (November, 12 1968)

Li, N.N. and Shrier, A.L. (1972). Liquid Membrane Water Treating. *Recent Dev. In Sep. Sci.*, ed. N.N. Li. Baca Raton, FL: CRC Press. 1: 163-174.

Li, Q-M., Liu, Q., and Wei, X-J. (1996). Separation Study of Mercury Through an Emulsion Liquid Membrane. *Talanta*. 43: 1837-1842.

Li, Q-M., Liu, Q., Li, K., and Tong, S. (1997). Separation Study of Cadmium Through an Emulsion Liquid Membrane. *Talanta,* 44: 657-662.

Li, Q-M., Liu, Q., Zhang,Q-F., Wei, X-J., and Guo, J-Z.. (1998). Separation Study of Cadmium through an Emulsion Liquid Membrane Using Triisooctylamine as Mobile Carrier. *Talanta*. 46: 927-932.

Li, W.X. and Shi Y.J. (1993). Water-Permeation Swelling of Emulsion Liquid Membrane. *Sep. Sci. Technol*. 28: 241-254.

Lin, C.C. and Long, R.L. (1997). Removal of Nitric Acid by Emulsion Liquid Membrane: Experimental Results and Model Prediction. *J. Membr. Sci*. 134: 33-45.

Lin, C.C. (1996). *Batch and Column Extraction by Emulsion Liquid Membrane Systems*. New Mexico State University: PhD Dissertation.

Lin, Z. W. (2001). *Surfactants as Applied to Penetrant Testing*. The American Society for Nondestructive Testing.

Lissant, K.J. (1983). Demulsification: Industrial Application*: Surfactant Science Series*, Vol. 13: Chapter 1. New York: Marcel Dekker Pub. 1-38.

Lo, T. C., Baird, M. H. I, and Hanson, C. (1983). *Handbook of Solvent Extraction*, Part IIIA and IIIB: John Wiley. 517-629.

Long, R. L. and Lin, C. C. (1995). Numerical Simulation and Design for Continuous Flow Extraction of Emulsion Liquid Membrane. *Dev. Chem. Eng. Mini. Proc*. 3(3/4): 177-186.

Lonsdale, H. K. (1982). The Growth of Membrane Technology. *J. Membr. Sci*. 10: 81-181.

Lorbach, D. and Marr, R. (1987). Emulsion Liquid Membranes Part II: Modelling Mass Transfer of Zinc with Bis(2-ethylhexyl)dithiophosphoric Acid. *Chem. Eng. Process*. 21: 83-93.

Lu, G., Lu, Q., and Li, P. (1997). Break-down of Liquid Membrane Emulsion under High Electric Field. *J. Membr. Sci*. 128: 1-6.

Luo, G.S., Pan, S., Liu, J.G., and Dai, Y.Y. (2001). Liquid-liquid Phase Equilibrium under External Electric Fields. *Sep. Sci. Technol*. 36: 2799-2809.

Mahmoud, M.H. H., Nakamura, S., and Akiba, K. (1996). Separation of Molybdenum(VI) and Tungsten(VI) Through a Supported Liquid Membrane Impregnated with Trioctylammonium Chloride. *Sep. Sci. Technol*. 31(20): 2763-2775.

Mahn, T. N. and Kopunec, R. (1992). Carrier-Mediated Transport of Rare Earth Elements Through Liquid Membranes: Transport of Sc, Y, Ce, Eu, Gd, Tm, Yb Through Supported Liquid Membrane Containing TOPO in n-dodecane. *J. Radioanal. Nucl. Chem*. 159(2): 219-231.

Makryaleas, K., Scheper, T., Schugerl, K., and Kula, M.R. (1985). *Chem. Ing. Tech*. 57: 362-363.

Marchese, J., Campderros, M. E., and Acosta, A. (1995). Transport and Separation of Cobalt, Nickel and Copper Ions with Alamine Liquid Membranes. *J. Chem. Technol. Biotechnol*. 64: 293.

Marr, R. (1984). Pilot Plant Studies of Liquid Membrane Separation. *Proceeding of Eng. Found. Conf. On New Directions in Separation technology*. Davos, Switzerland.

Marr, R. and Kopp, A. (1982). Liquid Membrane Technology – A Survey of Phenomena, Mechanisms and Models. *Int. Chem. Eng*. 22(1): 44-60.

Marr, R.J. and Draxler, J. (1992). Applications. In: W.S. Winston Ho, K.K. Sirkar Eds. *Membrane Handbook*. New York: Van Nostrand Reinhold. 701-717.

Mason, L.F.A. (1979). *Photographic Processing Chemistry*. 3th Edi. London: Focal Press.

Matsumoto, S. and Kohda, M. (1980). The Viscosity of W/O/W Emulsion: An Attempt to estimate the Water Permeation Coefficient of the Oil Layer from the Viscosity Changes in Diluted Systems on Aging Under Osmotic Pressure Gradient, *J. Coll. Interf. Sci*. 73: 13-20

Matsumoto, S., Inoue, T., and Kohda, M. (1980). Water Permeability of Oil Layer in W/O/W Emulsion under Osmotic Pressure Gradients. *J. Coll. Interf. Sci*. 77: 555-563.

Matulevicius, E. S. and Li, N. N. (1975). Facilitated Transport Through Liquid Membranes. *Sep. Purif. Methods*. 4: 73-96.

Maysa, S. E. S. (2003). Uranium Extraction from Gattar Sulfate Leach Liquor Using Aliquat-336 in a Liquid Emulsion Membrane Process. *Hydrometallurgy*. 68(1-3): 51-56.

Mendoza, C. S. and Kamata, S. (1996). Silver Extraction for Pollution Control of Photographic Fixing Solution with Tetramethylthiuram Disulfide. *Bull. Chem. Soc. Jpn*. 69: 3499-3504.

Mendoza, S., Kamata, S. and Sodeyama, K. (1996). Thiuram Sulfides as a Reagent for the Solvent Extraction of Silver. *Analy. Sci.*. 12: 969-972.

Mihaylov, I. and Distin, P.A. (1992). Gallium Solvent Extraction in Hydrometallurgy: An Overview. *Hydrometallurgy*. 28: 13-27.

Mojtaba, S. and Mohammad, H. M. (2000). Highly Efficient and Selective Membrane Transport of Silver(I) Using Hexathia-18-crown-6 as a Specific Ion Carrier. *Sep. Purif. Technol*. 20: 147-153.

Mok, Y.S. and Lee, W.K. (1994). Water Transport in Water-Oil-Water Liquid Emulsion Membrane System for the Separation of Latic Acid. *Sep. Sci. Technol*. 29: 743-764.

Molinari, R., Drioli, E., and Pantano, G. (1989). Stability and Effect of Diluents in Supported Liquid Membranes for Cr(III), Cr(VI), and Cd(II) Recovery. *Sep. Sci. Technol*. 24: 1015-1032.

Murry K.J. and Bouboulis C.J. (1973), *Eng. Min. J*. 174(7): 74-79.

Myers, D. (1988). *Surfactant science and Technology*. New York: VCH Publishers.

Nakashio, F. (1993). Recent Advances in Separation of Metals by Liquid Surfactant Membranes. *J. Chem. Eng. Jpn*. 26: 123-133.

Narishman, G., Ramkrihna, D., and Gupta, G.P. (1980). Analysis of Drop Size Distribution in Lean Liquid-Liquid Dispersions. *AIChE. J*. 26(6): 991-1000.

Nishihama, S., Hirai, T., and Komasawa, I. (2001). Review of Advanced Liquid-Liquid Extraction Systems for the Separation of Metals by a Combination of Conversion of the Metal Species with Chemical Reaction. *Ind. Eng. Chem. Res*. 40: 3085-3091.

Noble, R.D. and Way, J.D. (1987). *Liquid Membranes, Theory and Applications*. ACS Symposium Series. Washington, DC: ACS.

Ohto, K., Fujimoto, Y., and Inoue, K. (1999). Stepwise Extraction of Two Lead Ions with a Single Molecule of calyx[4]arene tetracarboxylic Acid. *Anal. Chim. Acta*. 387: 61-69.

Ohto, K., Murakami, E., Shinohara, T., Shiratsuchi, K., Inoue, K., and Iwasaki, M. (1997a). Selective Extraction of Silver(I) Over Palladium(II) with Ketonic Derivatives of Calixarenes from Highly Concentrated HNO_3. *Anal. Chim. Acta*. 341: 275-283.

Ohto, K., Yamaga, H., Murakami, E., and Inoue, K. (1997b). Specific Extraction Behavior of Amide Derivative of Calyx [4] arene for Silver (I) and Gold (III) Ions from Highly Acidic Chloride Media. *Talanta*. 44: 1123-1130.

Ortiz, I., Galan, B., and Irabien, A. (1996). Kinetic Analysis of the Simultaneous Non-dispersive Extraction and Back-extraction of Chromium(VI). *Ind. Eng. Chem. Res*. 35: 1369-1377.

Ostberg, G., Bergenstahl, B., and Hulden, M. (1995). Influence of Emulsifier on the Formation of Alkyd Emulsions, A. Physicochemical and Engineering Aspects. *Colloids Surf*. 94(2-3): 161-171.

Ouchi, M., Shibutani, Y., Yakabe, K., Shono, T., Shintani, H.,Yoneda, A., Hakushi, T., and Weber, E. (1999). Silver and Thallium(I) Complexation with Dibenzo-16-crown-4. *Bioorganic & Medicinal Chemistry*. 7(6): 1123-1126.

Oza, K. P. and Frank, S.G. (1989). Drug Release from Emulsions Stabilized by colloidal Microcrystalline Cellulose. *J. Disper. Sci. Technol*. 10(2): 187-210.

Paiva, A. P. (1993). Solvent Extraction and Related Studies on Silver Recovery From Aqueous Solutions. *Sep. Sci. Technol*. 28(4): 947-1008.

Patnaik, P. R. (1995). Liquid Emulsion Membranes: Principles, Problems and Application in Fermentation Processes. *Biotechnology Advances*. 13(2): 175-208.

Pearson, R. G. (1963). Hard and soft acids and bases. *J. Am. Chem. Soc*. 85: 3533-3543.

Preston, J.S. (1985). Solvent Extraction of Metal by Carboxylic Acids. *Hydrometallurgy*. 14: 171-188.

PRO-ACT (1995). Fact sheet of Silver Recovery from Photographic and Imaging Wastes: Technical Report.

Rajdip, B., Avijit, B., Siddartha, D., and Shyamal, K. S. (1998). A New Model of Batch-Extraction in Emulsion Liquid Membrane: Simulation of Globule–Globule Interaction and Leakage. *Chem. Eng. Sci*. 53(15): 2799-2807.

Rautenbach, R. and Machhammer, O. (1988). Modeling of Liquid membrane Separation Processes. *J. Membr. Sci*. 36: 425-444.

Reed, D. L., Bunge, A. L., and Noble, R. D. (1987). Influence of Reaction Reversibility on Continuous-Flow Extraction by Emulsion Liquid Membrane. In: *Liquid Membranes: Theory and Applications*. Noble R. D., Way J. D., Eds. Washington D. C.: American Chemical Society.

Reis, M. T. A. and Carvalho, J.M.R. (2004). Modeling of Zinc Extraction from Sulphate Solutions with Bis(2-ethylhexyl)thiophosphoric Acid by Emulsion Liquid Membranes. *J. Membr. Sci*. 237: 97-107.

Reis, M.T.A. and Carvalho, J.M.R. (1993). Recovery of Zinc from Industrial Effluent by Emulsion Liquid Membranes. *J. Membr. Sci*. 84: 201-211.

Ritcey, G.M. and Ashbrook, A.W. (1984). *Solvent Extraction: Principles and Applications to Process Metallurgy*. Part I. Amsterdam: Elsevier Science Publisher B.V.

Ritcey, G.M. and Lucas, B.H. (1974). *Proceedings International Solvent Extraction Conference ISEC'74*. Soc. Chem. Ind. London. 3: 2438.

Rohm and Haas: A Specialty Chemical Company (2003). *Ion Exchange Resins-Industrial Process-Silver Recovery from Photographic Baths.*

Rosell, A., Palet, C., and Valiente, M. (1997). Selective Separation and Concentration of Vanadium(V) by a Chemical Pumping Hollow-Fiber Supported Liquid Membrane. *Anal. Chim. Acta*. 349(1-3): 171.

Rosen, M.J. (1978). *Surfactant and Interfacial Phenomena*. New York: Wiley-Interscience Publication.

Rumscheidt, F.D. and Mason, S.G. (1961). Particle Motions in Sheared Suspentions: XI. Internal Circulation in Fluid Droplets. *J. Coll. Interf. Sci*. 16: 210-237.

Rydberg, J., Musikas, C., and Choppin, G.R. (1992). *Principles and Practices of Solvent Extraction*. New York: Macel Dekker Inc.

Saha, S. and Chakma, A. (1992). Separation of CO_2 from Gas Mixtures with Liquid Membranes. *Energy Conversion and Management*. 33(5-8): 413-420.

Saidi, H. and Ariffin, A. (1994). *Reduction of Waste from Photographic Shops*. Universiti Teknologi Malaysia: Technical Report.

Saito, K., Taninaka, I., Murakami, S., and Muromatsu, A. (1998). Extraction Behaviour of Copper(II) and Silver(I) with a Thiacrown ether carboxylic Acid 2-(3,6,10,13-tetrathiacyclotetradec-1-oxy)hexanoic Acid. *Talanta*. 46(5): 1187-1194.

Saji, J., Rao, T.P, Iyer, C. S. P., and Reddy, M. L. P. (1998). Extraction of Iron (III) from Acidic Chloride Solutions by Cyanex 923. *Hydrometallurgy*. 49: 289-296.

Sanuki, S., Yata, M., and Majima, H. (1999). Stripping of Silver from Primene JMT Loaded with Silver Thiocyanate Complexes. *Hydrometallurgy*. 52(2): 123-135.

Scheper, T., Likidis, Z., Makryaleas, K., Nowottny, Ch., and Schügerl, K. (1987). Three Different Examples of Enzymatic Bioconversion in Liquid Membrane Reactors**.** *Enzyme Microbial Technol*. 9(10): 625-631

Sekine, T. and Hasegawa, Y. (1977). *Solvent Extraction Chemistry, Fundamental and Application*. New York: Marcel Dekker Inc.

Sharad, N.D., and Purushottam, M.D. (2001). Comparative Study of the Determination of Platinum by Extraction with Cyanex 923 and Cyanex 471X from Bromide media. *J. Chem. Tech. Biotechnol*. 76: 1227-1234.

Shen, J. Q., Yin, W. P., Zhao, Y. X., and Yu, L. J. (1996). Extraction of Alanine Using Emulsion Liquid Membranes Featuring a Cationic Carrier. *J. Membr. Sci*. 120: 45-53.

Shiau, C-Y. (1991). Analysis of Transport Rate of Zinc Extraction Through Liquid Surfactant Membrane. *Sep. Sci. Technol*. 26: 1519-1530.

Shiau, C-Y. and Jung, S-W. (1993). Selective Extraction of Metal Ions Through Liquid Surfactant Membranes. *J. Chem. Tech. Biotechnol*. 56: 27-33.

Shukla, J. P. and Misra, S. K. (1991). Carrier-mediated Transport of Uranyl Ions across Tributyl phosphate-Dodecane Liquid Membranes. *J. Membr. Sci*. 64: 93-102.

Sittig, M. (1980). *Metal and Inorganic Waste Reclaiming Encyclopedia*. Park Ridge, NJ: Noyes Data Corporation.

Sittig, M. (1973). *Pollutant Removal Handbook*. Park Ridge, NJ: Noyes Data Corporation.

Sjoblom, A. J. (1996). *Emulsion and Emulsion Stability*. Marcel Dekker.

Skelland, A.H.P. (1999). Non-newtonian Conversion Solves Problems of Stability, Permeability, and Swelling in Emulsion Liquid Membrane. *J. Membr. Sci*. 158: 1-15.

Smith, D. R., Lander, R. J., and Quinn, J. A. (1977). Carrier-Mediated Transport in Synthetic Membranes. In: Li, N. N. (Ed). *Recent Development in Separation Science*. Vol.3, Cleveland, Ohio: CRC Press.

Smith, I.C. and Bonnie, L.C. (1977). *'Silver', in Trace Metal in the Environment*. Vol. 2. Michigan: Ann Arbor Science Publisher Inc.

Sole, K. C. and Hiskey, J. B. (1995). Solvent extraction of copper by Cyanex 272, Cyanex 302 and Cyanex 301. *Hydrometallurgy*. **37**: 129-147.

Sole, K. C., Ferguson, T. L., and Hiskey, J.B. (1994). Solvent Extraction of Silver by Cyanex 272, Cyanex 302 and Cyanex 301. *Solv. Extr. Ion Exch*. 12(5): 1033-1050.

Srinivasan, M.P. and Stroeve, P. (1986). Sub drop Ejection from Double Emulsion Drops in Shear Flow. *J. Memb. Sci*. 26: 231-236.

Stary, J. (1963). *The Solvent of Metal Chetales*. New York: Pergamon Press.

Strathman, H. (2001). Membrane Separation Processes: Current Relevance and Future Opportunities. *AIChE J*. 47: 1077-1087.

Strestrom, S. (1992). Solvent Extraction Conference 1990. Ed by T. Sekine. New York: Elsevier Science Publishers. 943-948.

Stroeve, P. and Varanasi, P.P. (1984). An Experimental study on Double Emulsion Drop Breakup in Uniform Shear Flow. *J. Coll. Interf. Sci*. 99(2): 360-373.

Sanuki, S., Yata, M., and Majima, H. (1999). Stripping of Silver from Primene JMT Loaded with Silver Thiocyanate Complexes. *Hydrometallurgy*. 52(2): 123-135.

Szpakowska, M. and Nagy, O. B. (1997). Stability of Supported Liquid Membranes Containing Acorga P-50 as Carrier. *J. Membr. Sci*. 129: 251-261.

Szpakowska, M. (1996). Coupled Transport of Copper Through Different Types of Liquid Membranes Containing Acorga P-50 as Carrier. *J. Membr. Sci*. 109: 77-86.

Szpakowska, M. and Nagy, O.B. (1991). Membrane Material Effect on Copper Coupled Transport Through Liquid Membranes. *J. Membr. Sci*. 64: 129-143.

Tait, B. K. (1993). Cobalt-Nickel Separation: The Extraction of Cobalt (II) and Nickel (II) by Cyanex 301, Cyanex 302 and Cyanex 272. *Hydrometallurgy*. 32: 365-372.

Takahashi, K. Ohtsubo, F., and Takeuchi, H. (1981). A Study of the Stability of (W/O/W) Type Emulsion Using a Tracer Technique. *J. Chem. Eng. Jpn*. 14: 416-418.

Takeo, A. and Hiroshi, T. (1990). *Liquid Membranes: Chemical Applications*. Boca Raton, Florida: CRC Press, Inc.

Taylor, S.E. (1988). Investigation into the Electrical and Coalescence Behaviour of Water-in-Crude Oil Emulsions in High Voltage Gradients. *Colloids Surf*. 29: 29-51.

Teramoto, M. and Matsuyama, H. (1986). Effect of Facilitated Diffusion in Internal Aqueous Droplets on Effective Diffusivity and Extraction Rate of Phenol in Emulsion Liquid Membranes. *J. Chem. Eng. Jpn.* 19(5): 469-472.

Teramoto, M., Qiangfa, H., Taisuke, M., and Hideto, M. (1999). Facilitated Transport of SO_2 Through Supported Liquid Membrane using Water as a Carrier. *Sep. Purif. Technol*. 16(2): 109-118.

Teramoto, M., Sakai, T., Yanagawa, K., Ohsuga, M., and Miyake Y. (1983). Modeling of the Permeation of Copper through Liquid Surfactant Membrane. *Sep. Sci. Technol.* 18: 735-764.

Teramoto, M., Takihana, H., Shibutani, M., Yuasa, T., Miyake, Y., and Teranishi, H. (1981). Extraction of Amine by W/O/W Emulsion. *J. Chem. Eng. Jpn*. 14: 122-128.

Teramoto, M., Takihana, H., Shibutani, M., Yussa, T., and Hara, N. (1983). Extraction of Phenol and Cresol by Liquid Surfactant Membranes. *Sep. Sci. Technol*. 18: 397-420.

Thien, M.P. and Hatton, T.A. (1988). Liquid Emulsion Membrane and Their Applications in Biochemical Processing. *Sep. Sci. Technol*. 23: 819.

Thien, M.P., Hatton, T.A., and Wang, D.I.C (1988). Separation and Concentration of Amino Acids using Liquid Emulsion Membranes. *Biotechnol. Bioeng*. 32: 604-615.

Thorn, G.D. and Ludwig, R.A. (1962). The Dithiocarbamates and Related Compounds. Amsterdam-New York: Elsevier Publishing Co. 43-271.

Tutkun, O., Demircan, N., and Kumbasar, R.A. (1999). Extraction of Germanium from Acidic Leach Solutions by Liquid Membrane Technique. *Clean Prod. Processes*. 1: 148-153.

Volkel, W., Halwachs, W., and Schugerl, K. (1980). Copper Extraction by Means of a Liquid Surfactant Membrane Process. *J. Membr. Sci*. 6: 19-31.

Volkel, W., Poppe, W., Halwachs, W., and Schugerl, K. (1982). Extraction of Free Phenols from Blood by a Liquid Membrane Enzyme Reactor. *J. Membr. Sci*. 11: 333-347.

Wan, Y. and Zhang, X. (2002). Swelling Determination of W/O/W Emulsion Liquid Membrane. *J. Membr. Sci*. 196: 185-201.

Wang, K. C. (1984). *Mathematical Modeling of Carrier Mediated Mass Transfer Through Liquid Membrane Systems*. New Jersey Institute of Technology: PhD. Thesis.

Wang, S.S., Lee, C.J., and Chan, C.C. (1994). Demulsification of Water-in-Oil Emulsions by Use of a High Voltage A.C. Field. *Sep. Sci. Technol*. 29: 159-170.

Wright, J. B., Nilsen, D. N., Hundley, G., and Galvan, G. J. (1995). Field Test of Liquid Emulsion Membrane Technique for Copper Recovery from Mine Solutions. *Min. Eng*. 8: 549-556.

Yan, J. and Pal, R. (2001). Osmotic Swelling Behavior of Globules of W/O/W Emulsion Liquid Membranes. *J. Membr. Sci*. 190: 79-91.

Yan, Z., Li, S-Y., Wang, L-C., and Yang, F-Y. (1990). Demulsification of Liquid Membranes in Electric Fields. *Water Treatment*. 5: 1-6.

Yang, X. and Fane, T. (1997). Effect of Membrane Preparation on the Life-time of Supported Liquid Membranes. *J. Membr. Sci*. 133: 269-273.

Ye, Z.F., Wang, Y.P., Liu, Y.S., Jiang, Z.L., Shen, X., Zhu, L.G., and Shi, X.F. (1999). Transport of Na^+, K^+ Ions in a Bubbling Pseudo-Emulsion Liquid Membrane System with P-tert-butylcalixarenes as carrier. *J. Membr. Sci*. 163: 367-372.

Yi, J. and Taviarides, L. L. (1995). Modeling Chemically Active Liquid Membranes in Tubular Inorganic Supports. *AIChE J*. 41(6): 1403-1415.

Yun, C. H., Prasad, R., Guha, A. K., and Sirkar, K. K. (1993). Hollow Fiber Solvent Extraction Removal of Toxic Heavy Metals from Aqueous Waste Streams. *Ind. Eng. Chem. Res*. 32(6): 1186-1195.

Zha, F. F. and Fell, C.J.D. (1995). Effect of Surface Tension Gradients on Stability of Supported Liquid Membranes. *J. Membr. Sci*. 107: 75-86.

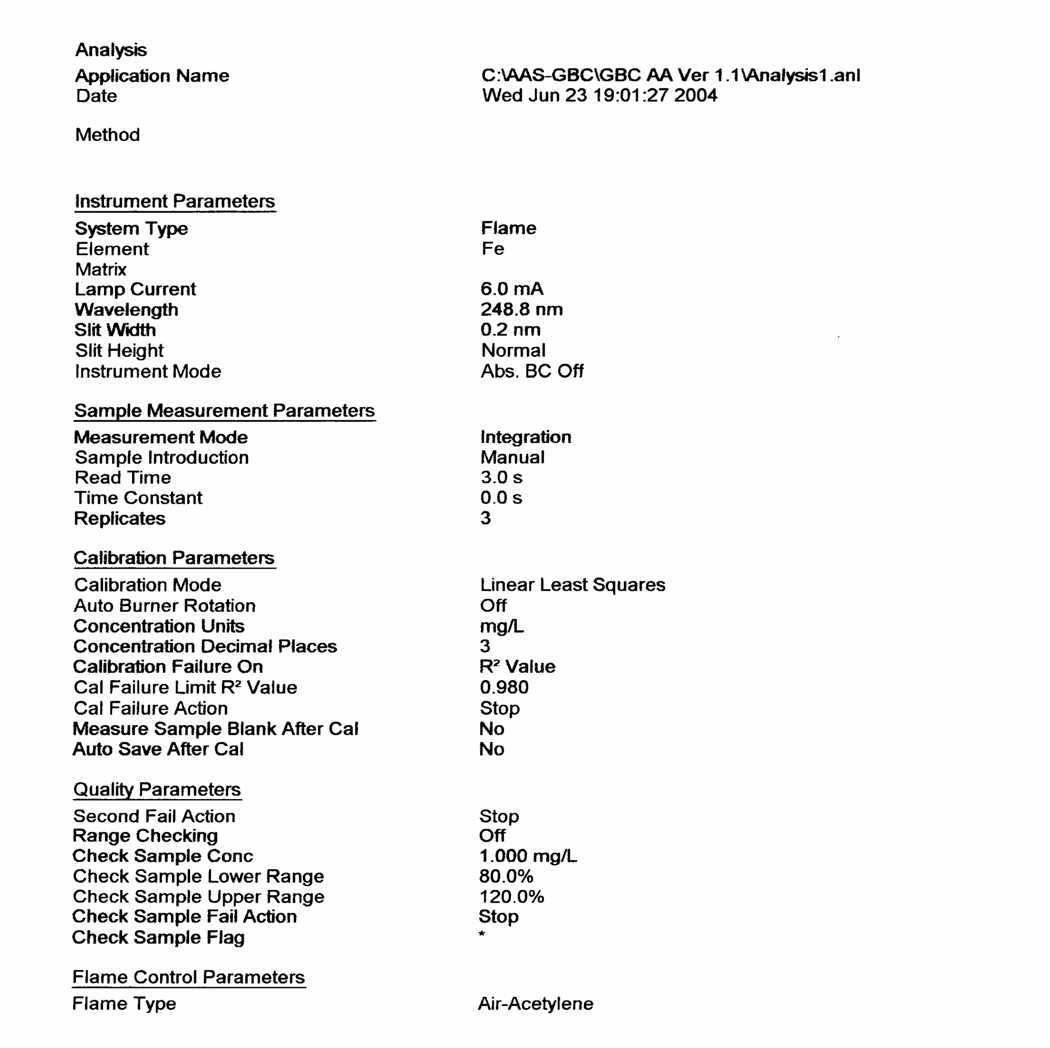
Zha, F. F., Fane, A. G., and Fell, C.J.D. (1995). Instability Mechanisms of Supported Liquid Membranes in Phenol Transport Process. *J. Membr. Sci*. 107: 59-74.

Zhou, D.W. (1996). *Emulsion Liquid Membrane Removal of Arsenic and Strontium from Wastewater*. New Jersey Institute of Technology: PhD dissertation.

Zouboulis, A. I. (1995). Silver Recovery from Aqueous Streams using Ion Flotation, *Min. Eng*. 8(12): 1477-1488.

APPENDIX A

QUANTITATIVE ANALYSIS REPORT: STANDARD OF AAS



Analysis

Application Name	C:\AAS-GBC\GBC AA Ver 1.1\Analysis1.anl
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Method

Instrument Parameters

System Type	Flame
Element	Fe
Matrix	
Lamp Current	6.0 mA
Wavelength	248.8 nm
Slit Width	0.2 nm
Slit Height	Normal
Instrument Mode	Abs. BC Off

Sample Measurement Parameters

Measurement Mode	Integration
Sample Introduction	Manual
Read Time	3.0 s
Time Constant	0.0 s
Replicates	3

Calibration Parameters

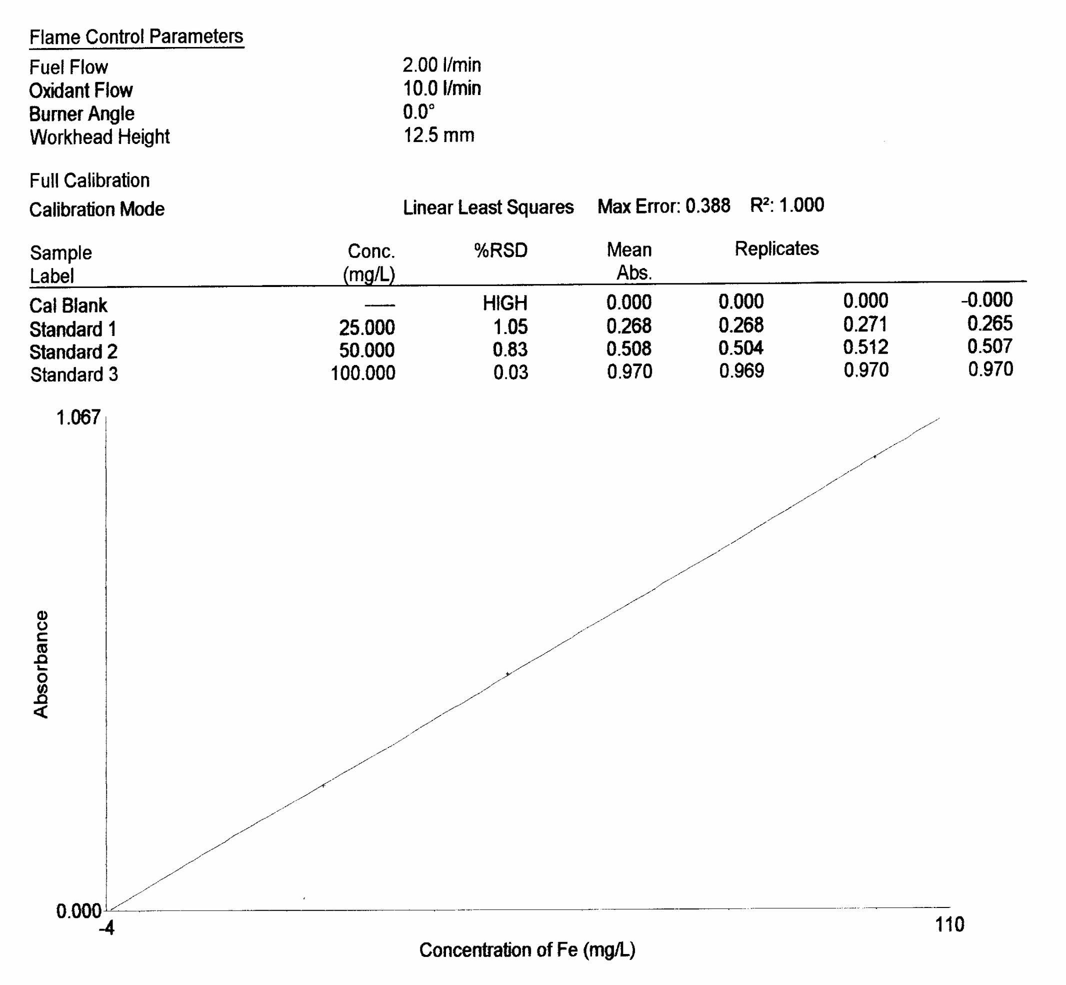
Calibration Mode	Linear Least Squares
Auto Burner Rotation	Off
Concentration Units	mg/L
Concentration Decimal Places	3
Calibration Failure On	R^2 Value
Cal Failure Limit R^2 Value	0.980
Cal Failure Action	Stop
Measure Sample Blank After Cal	No
Auto Save After Cal	No

Quality Parameters

Second Fail Action	Stop
Range Checking	Off
Check Sample Conc	1.000 mg/L
Check Sample Lower Range	80.0%
Check Sample Upper Range	120.0%
Check Sample Fail Action	Stop
Check Sample Flag	*

Flame Control Parameters

Flame Type	Air-Acetylene



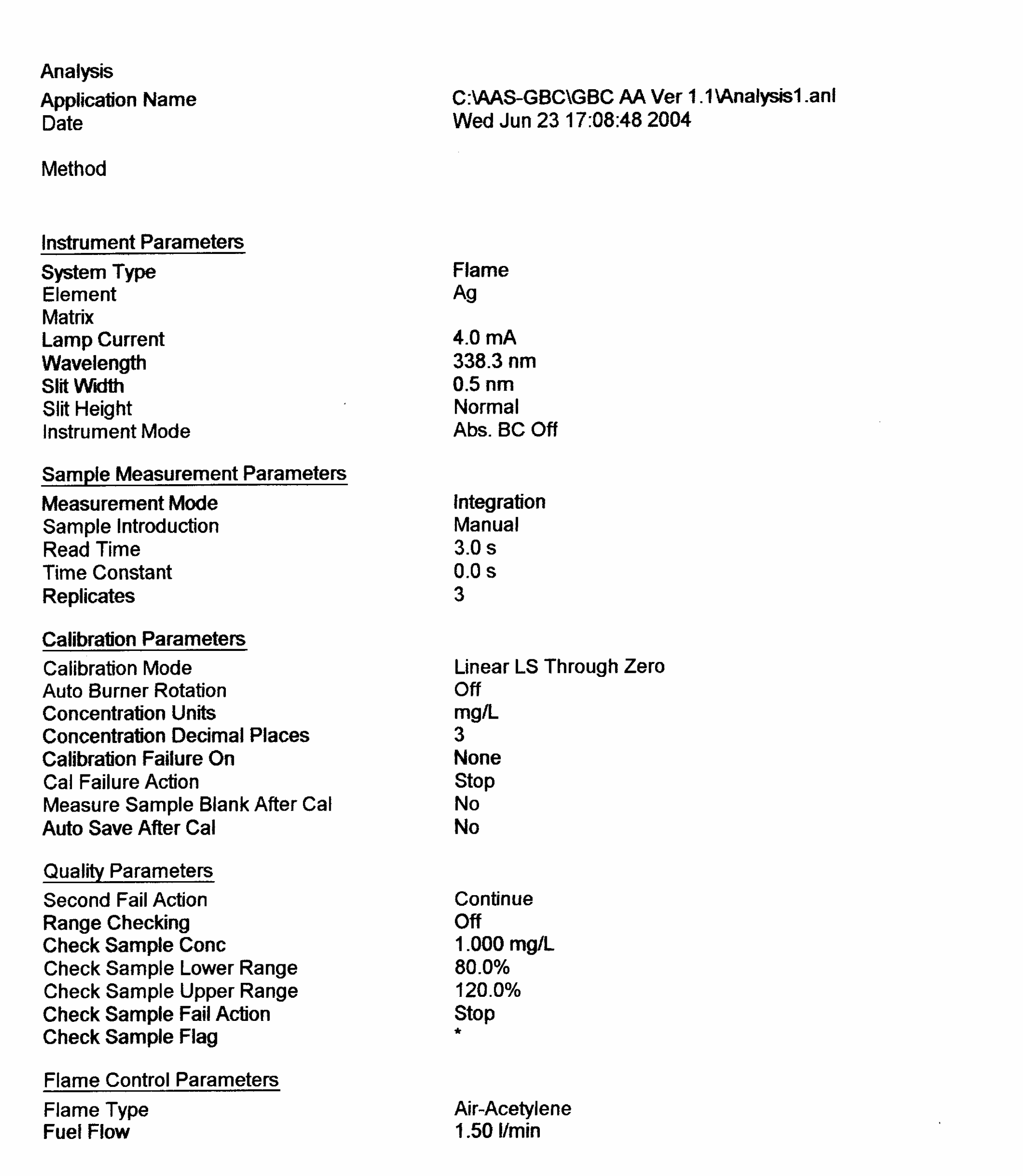
Flame Control Parameters

Fuel Flow	2.00 l/min
Oxidant Flow	10.0 l/min
Burner Angle	0.0°
Workhead Height	12.5 mm

Full Calibration

Calibration Mode Linear Least Squares Max Error: 0.388 R^2: 1.000

Sample Label	Conc. (mg/L)	%RSD	Mean Abs.	Replicates		
Cal Blank	—	HIGH	0.000	0.000	0.000	-0.000
Standard 1	25.000	1.05	0.268	0.268	0.271	0.265
Standard 2	50.000	0.83	0.508	0.504	0.512	0.507
Standard 3	100.000	0.03	0.970	0.969	0.970	0.970



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Analysis
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Date                                Wed Jun 23 17:08:48 2004

Method


Instrument Parameters
System Type                         Flame
Element                             Ag
Matrix
Lamp Current                        4.0 mA
Wavelength                          338.3 nm
Slit Width                          0.5 nm
Slit Height                         Normal
Instrument Mode                     Abs. BC Off

Sample Measurement Parameters
Measurement Mode                    Integration
Sample Introduction                 Manual
Read Time                           3.0 s
Time Constant                       0.0 s
Replicates                          3

Calibration Parameters
Calibration Mode                    Linear LS Through Zero
Auto Burner Rotation                Off
Concentration Units                 mg/L
Concentration Decimal Places        3
Calibration Failure On              None
Cal Failure Action                  Stop
Measure Sample Blank After Cal      No
Auto Save After Cal                 No

Quality Parameters
Second Fail Action                  Continue
Range Checking                      Off
Check Sample Conc                   1.000 mg/L
Check Sample Lower Range            80.0%
Check Sample Upper Range            120.0%
Check Sample Fail Action            Stop
Check Sample Flag                   *

Flame Control Parameters
Flame Type                          Air-Acetylene
Fuel Flow                           1.50 l/min
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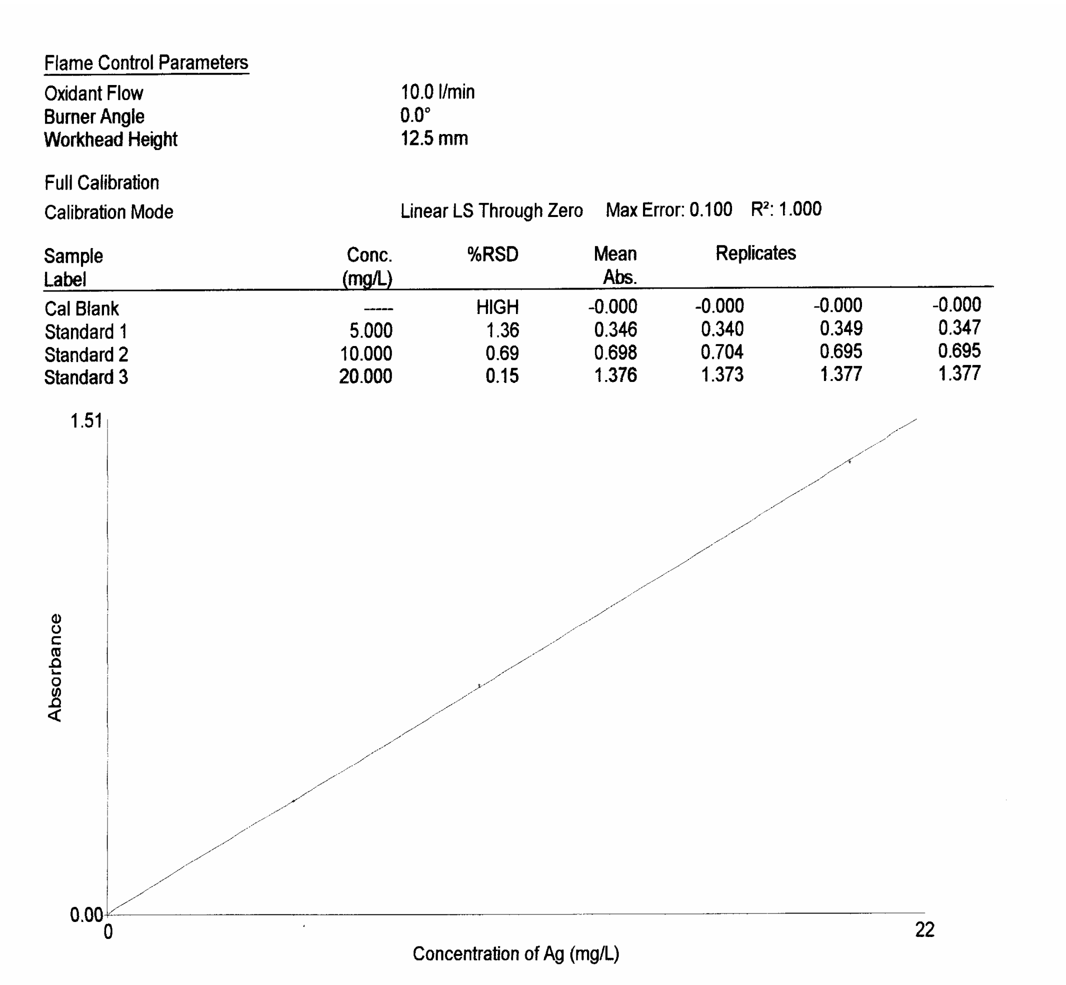

Flame Control Parameters

Oxidant Flow	10.0 l/min
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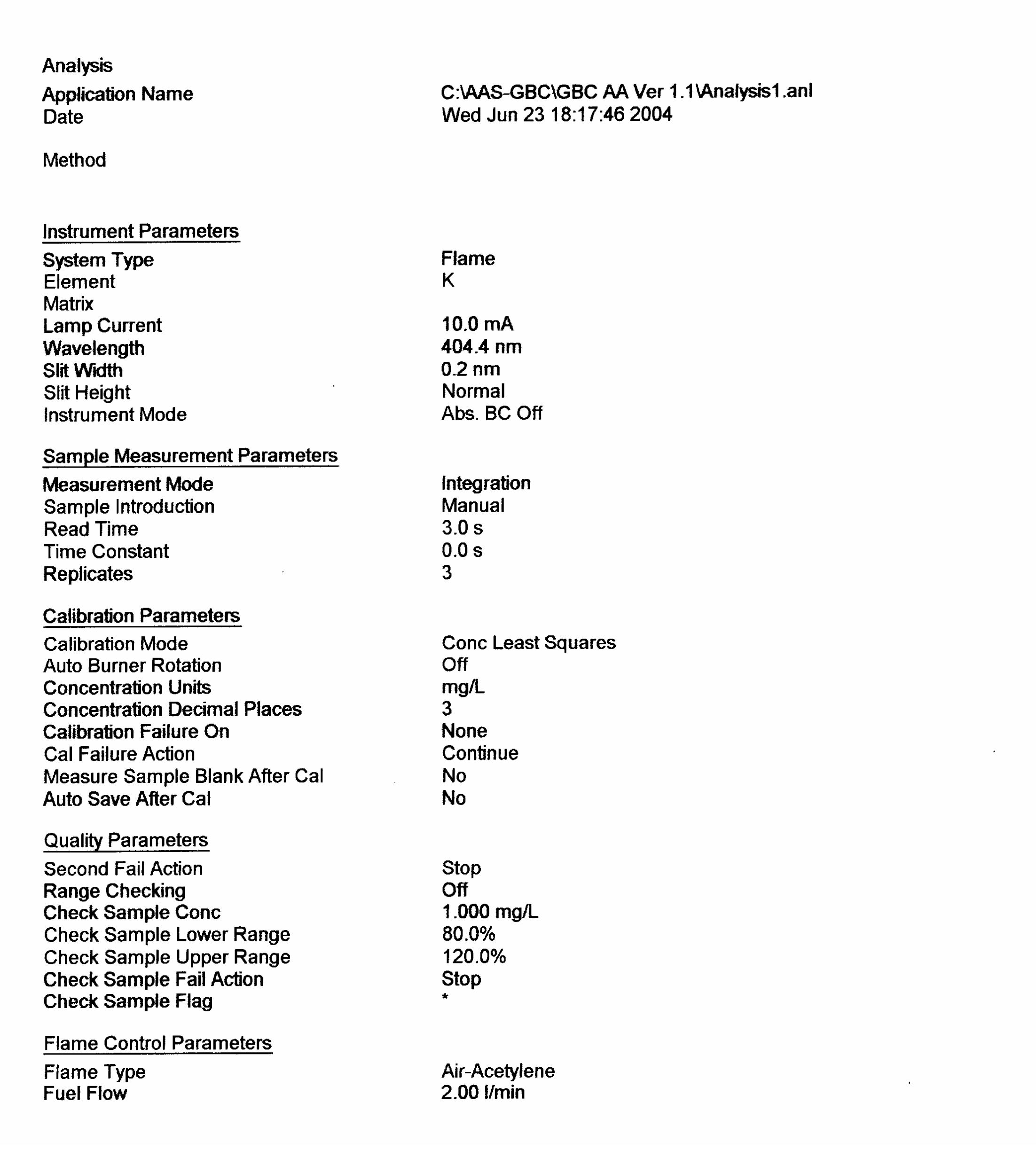
Workhead Height	12.5 mm

Full Calibration

Calibration Mode Linear LS Through Zero Max Error: 0.100 R^2: 1.000

Sample Label	Conc. (mg/L)	%RSD	Mean Abs.	Replicates		
Cal Blank	-----	HIGH	-0.000	-0.000	-0.000	-0.000
Standard 1	5.000	1.36	0.346	0.340	0.349	0.347
Standard 2	10.000	0.69	0.698	0.704	0.695	0.695
Standard 3	20.000	0.15	1.376	1.373	1.377	1.377



Analysis

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Date	Wed Jun 23 18:17:46 2004

Method

Instrument Parameters

System Type	Flame
Element	K
Matrix	
Lamp Current	10.0 mA
Wavelength	404.4 nm
Slit Width	0.2 nm
Slit Height	Normal
Instrument Mode	Abs. BC Off

Sample Measurement Parameters

Measurement Mode	Integration
Sample Introduction	Manual
Read Time	3.0 s
Time Constant	0.0 s
Replicates	3

Calibration Parameters

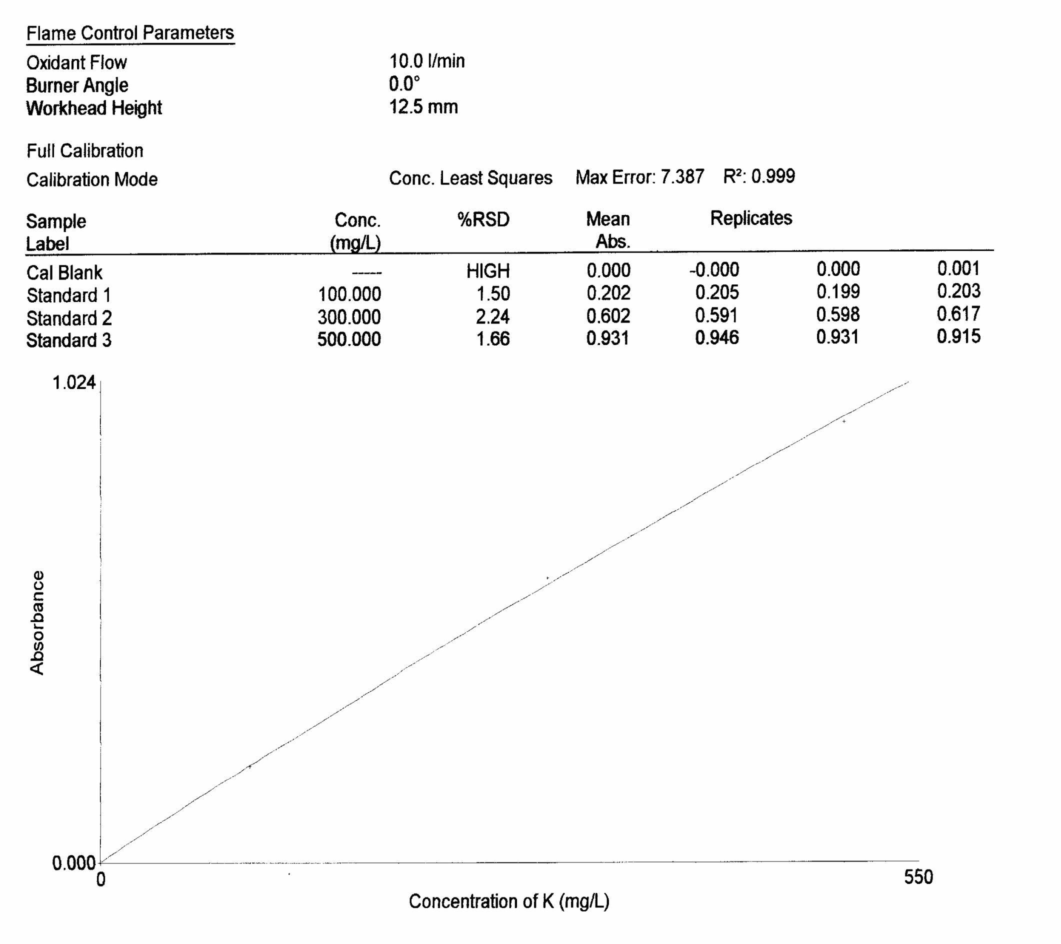
Calibration Mode	Conc Least Squares
Auto Burner Rotation	Off
Concentration Units	mg/L
Concentration Decimal Places	3
Calibration Failure On	None
Cal Failure Action	Continue
Measure Sample Blank After Cal	No
Auto Save After Cal	No

Quality Parameters

Second Fail Action	Stop
Range Checking	Off
Check Sample Conc	1.000 mg/L
Check Sample Lower Range	80.0%
Check Sample Upper Range	120.0%
Check Sample Fail Action	Stop
Check Sample Flag	*

Flame Control Parameters

Flame Type	Air-Acetylene
Fuel Flow	2.00 l/min



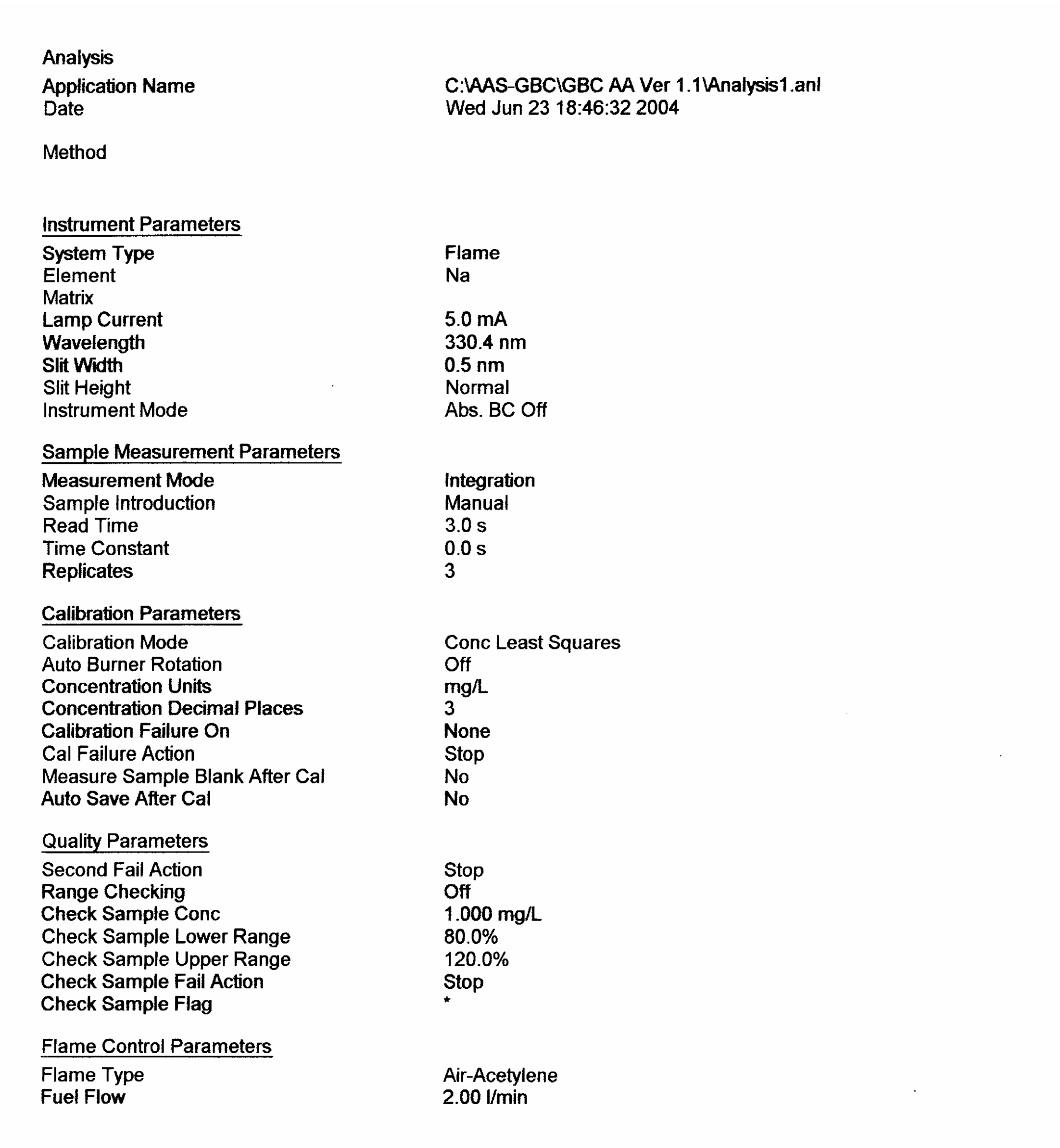
Flame Control Parameters

Oxidant Flow 10.0 l/min
Burner Angle 0.0°
Workhead Height 12.5 mm

Full Calibration

Calibration Mode Conc. Least Squares Max Error: 7.387 R^2: 0.999

Sample Label	Conc. (mg/L)	%RSD	Mean Abs.	Replicates		
Cal Blank	-----	HIGH	0.000	-0.000	0.000	0.001
Standard 1	100.000	1.50	0.202	0.205	0.199	0.203
Standard 2	300.000	2.24	0.602	0.591	0.598	0.617
Standard 3	500.000	1.66	0.931	0.946	0.931	0.915



Analysis

Application Name	C:\AAS-GBC\GBC AA Ver 1.1\Analysis1.anl
Date	Wed Jun 23 18:46:32 2004

Method

Instrument Parameters

System Type	Flame
Element	Na
Matrix	
Lamp Current	5.0 mA
Wavelength	330.4 nm
Slit Width	0.5 nm
Slit Height	Normal
Instrument Mode	Abs. BC Off

Sample Measurement Parameters

Measurement Mode	Integration
Sample Introduction	Manual
Read Time	3.0 s
Time Constant	0.0 s
Replicates	3

Calibration Parameters

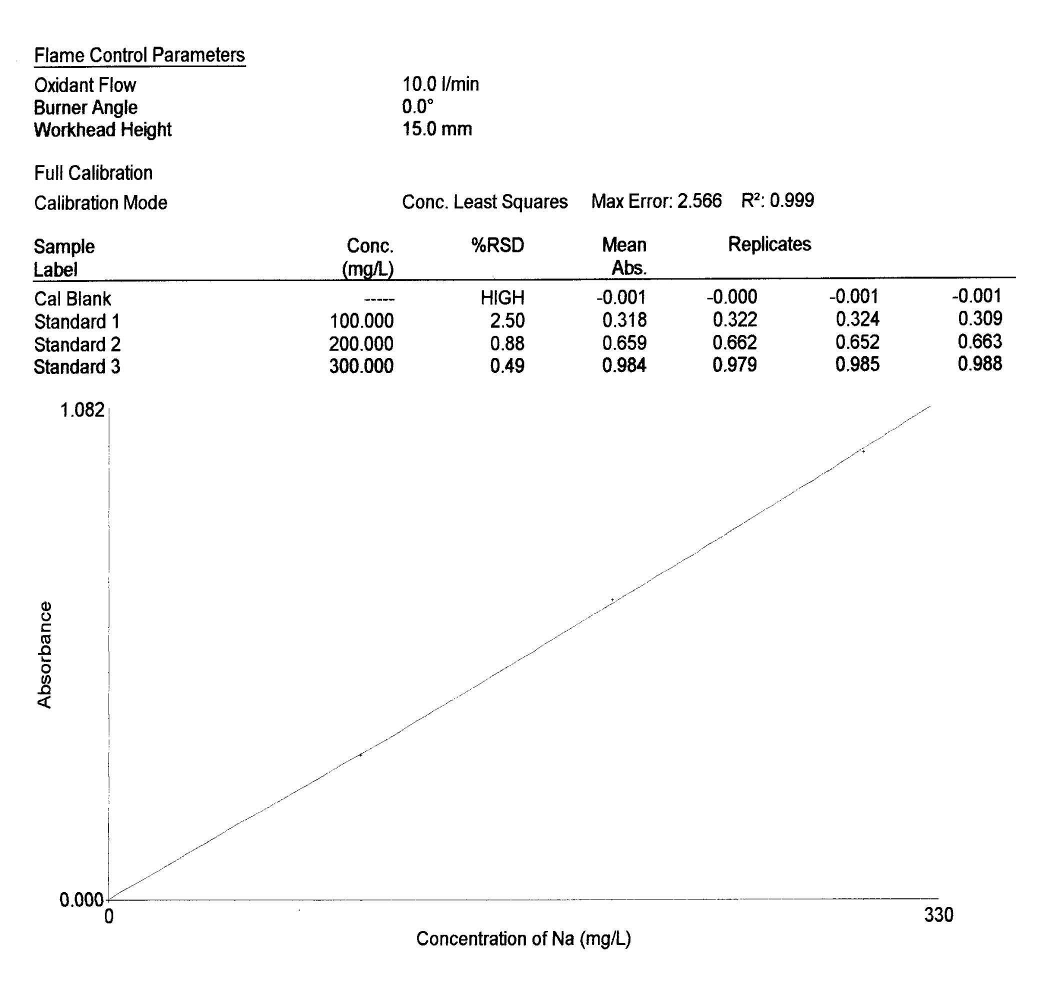
Calibration Mode	Conc Least Squares
Auto Burner Rotation	Off
Concentration Units	mg/L
Concentration Decimal Places	3
Calibration Failure On	None
Cal Failure Action	Stop
Measure Sample Blank After Cal	No
Auto Save After Cal	No

Quality Parameters

Second Fail Action	Stop
Range Checking	Off
Check Sample Conc	1.000 mg/L
Check Sample Lower Range	80.0%
Check Sample Upper Range	120.0%
Check Sample Fail Action	Stop
Check Sample Flag	*

Flame Control Parameters

Flame Type	Air-Acetylene
Fuel Flow	2.00 l/min



Flame Control Parameters

Oxidant Flow 10.0 l/min
Burner Angle 0.0°
Workhead Height 15.0 mm

Full Calibration

Calibration Mode Conc. Least Squares Max Error: 2.566 R^2: 0.999

Sample Label	Conc. (mg/L)	%RSD	Mean Abs.	Replicates		
Cal Blank	-----	HIGH	-0.001	-0.000	-0.001	-0.001
Standard 1	100.000	2.50	0.318	0.322	0.324	0.309
Standard 2	200.000	0.88	0.659	0.662	0.652	0.663
Standard 3	300.000	0.49	0.984	0.979	0.985	0.988

APPENDIX B

DATA COLLECTION FOR ELM EXTRACTION PROCESS

Table B1: Data of extraction time effect (Experimental conditions: [Cyanex 302] = 0.05M, diluents = kerosene, [Span 80] = 5% (w/v), sample = real photographic waste, and stripping agent = 1 M thiourea in 1 M H_2SO_4)

Time	Original (ppm)	Aqueous (ppm)	amount extracted	% extracted	Ce/Co	%B-up
0	2054.561	2054.561	0	0.00	1.00	0
1	2054.561	300.485	1754.076	85.37	0.15	7
3	2054.561	33.959	2020.602	98.35	0.02	8
5	1968.275	41.539	1926.736	97.89	0.02	10
7.5	2010.316	34.45	1975.866	98.29	0.02	10
10	1968.275	50.698	1917.577	97.42	0.03	10
15	1968.275	38.449	1929.826	98.05	0.02	8
20	2054.561	116.826	1937.735	94.31	0.06	0
25	2702	815.6	1886.4	69.81	0.30	-6
30	2702	1016	1686	62.40	0.38	-8
35	2702	1022	1680	62.18	0.38	-10
40	2702	1042	1660	61.44	0.39	-18

Table B2: Data of effect of thiourea concentration (Experimental conditions: [Cyanex 302] = 0.05M, diluent = kerosene, [Span 80] = 5% (w/v), sample = real photographic waste, and stripping agent : (a) 0.5 M thiourea in 1 M H_2SO_4, (b) 1.0 M thiourea in 1 M H_2SO_4 and (c) 1.5 M thiourea in 1 M H_2SO_4.

(a) 0.5 M thiourea in 1 M H_2SO_4

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2388.925	2388.925	0.00	1.00
1	2388.925	1043.491	56.32	0.44
3	2388.925	708.748	70.33	0.30
5	2388.925	659.162	72.41	0.28
7.5	2388.925	671.978	71.87	0.28
10	2388.925	663.448	72.23	0.28
15	2388.925	786.899	67.06	0.33
20	2388.925	944.591	60.46	0.40

(b) 1.0 M thiourea in 1 M H_2SO_4

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.29	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.024
20	2054.561	116.826	94.31	0.06

(c) 1.5 M thiourea in 1 M H_2SO_4

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2986.63	2986.63	0.00	1.00
1	2986.63	396.674	86.71	0.13
3	2986.63	121.961	95.92	0.04
5	2986.63	70.469	97.64	0.02
7.5	2986.63	66.503	97.77	0.02
10	2986.63	96.313	96.78	0.03
15	2986.63	113.757	96.19	0.04
20	2986.63	355.295	88.10	0.12

Table B3: Data of effect of acid concentration in thiourea solution (Experimental conditions: [Cyanex 302] = 0.05M, diluent = kerosene, [Span 80] = 5% (w/v), sample = real photographic waste, and stripping agent : (a) 1.0 M thiourea in 0.5 M H_2SO_4, (b) 1.0 M thiourea in 0.75 M H_2SO_4 and (c) 1.0 M thiourea in 1.5 M H_2SO_4

(a) 1.0 M thiourea in 0.5 M H_2SO_4

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2200	2200	0.00	1.00
1	2200	1050.101	52.27	0.48
3	2200	927.468	57.84	0.42
5	2200	1269.675	42.29	0.58
7.5	2200	1376.188	37.45	0.63
10	2200	1370.953	37.685	0.62
15	2200	1427.149	35.13	0.65
20	2200	1546.976	29.68	0.70

(b) 1.0 M thiourea in 0.75 M H_2SO_4

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	3242	3242	0.00	1.00
1	3242	1800	44.48	0.56
3	3242	1275	60.67	0.39
5	3242	1078	66.75	0.33
7.5	3242	951	70.67	0.29
10	3242	979.6	69.78	0.30
15	3242	1790	44.79	0.55
20	3242	2448	24.49	0.76

(c) 1.0 M thiourea in 1.5 M H_2SO_4

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	3187.664	3187.664	0.00	1.00
1	3187.664	619.878	80.55	0.19
3	3187.664	125.955	96.05	0.04
5	3187.664	118.76	96.27	0.04
7.5	3187.664	70.987	97.77	0.02
10	3187.664	97.618	96.94	0.03
15	3187.664	175.6	94.49	0.06
20	3187.664	178.439	94.40	0.06

Table B4: Data of Effect of Varies Concentration of Cyanex 302 (Experimental conditions: Agitation speed = 250 rpm, diluent = kerosene, [Span 80] = 5% (w/v), sample = real photographic waste, and stripping agent = 1.0 M thiourea in 1.0 M H_2SO_4, [Cyanex 302] = (a) 0.01 M, (b) 0.03 M, (c) 0.05 M , and (d) 0.07 M.

(a) 0.01 M Cyanex 302

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2817.15	2817.15	0.00	1.00
1	2817.15	1822.243	35.32	0.65
3	2817.15	1178.16	58.18	0.42
5	2817.15	731.664	74.03	0.26
7.5	2817.15	479.033	83.00	0.17
10	2817.15	357.961	87.30	0.13
15	2817.15	228.117	91.90	0.08
20	2817.15	234.569	91.67	0.08

(b) 0.03 M Cyanex 302

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2875.873	2875.873	0.00	1.00
1	2875.873	929.671	67.67	0.32
3	2875.873	412.259	85.66	0.14
5	2875.873	179.996	93.74	0.06
7.5	2875.873	187.364	93.48	0.07
10	2875.873	129.075	95.51	0.04
15	2875.873	198.552	93.10	0.07
20	2875.873	241.037	91.62	0.08

(c) 0.05 M Cyanex 302

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1.00
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.29	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.02
20	2054.561	116.826	94.31	0.06

(d) 0.07 M Cyanex 302

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	6250.293	6250.293	0.00	1.00
1	6250.293	902.198	85.57	0.14
3	6250.293	192.377	96.92	0.03
5	6250.293	122.859	98.03	0.02
10	6250.293	167.11	97.33	0.03
15	6250.293	323.567	94.82	0.05
20	6250.293	373.968	94.02	0.06

Table B5: Data of effect of diluents in liquid membrane (Experimental conditions: [Cyanex 302] = 0.05 M, agitation speed = 250 rpm, [Span 80] = 5% (w/v), sample = real photographic waste, and stripping agent = 1.0 M thiourea in 1.0 M H_2SO_4, diluents = (a) Kerosene, (b) Toluene, and (c) n- Dodecane.

(a) Kerosene

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1.00
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.294	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.02
20	2054.561	116.826	94.31	0.06

(b) Toluene

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2852.47	2852.47	0.00	1.00
1	2852.47	1427.401	49.96	0.50
3	2852.47	921.645	67.69	0.32
5	2852.47	845.382	70.36	0.30
7.5	2852.47	1316.486	53.85	0.46
10	2852.47	1724.772	39.53	0.60
15	2852.47	2329.214	18.34	0.82
20	2852.47	3484.117	0.00	1.00

(c) n- Dodecane

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2811.006	2811.006	0.00	1.00
1	2811.006	1017.014	63.82	0.36
3	2811.006	522.189	81.42	0.19
5	2811.006	422.573	84.97	0.15
7.5	2811.006	517.106	81.60	0.18
10	2811.006	566.653	79.84	0.20
15	2811.006	618.582	77.99	0.22
20	2811.006	983.21	65.02	0.35

Table B6: Data of effect of surfactant concentration (Experimental conditions: [Cyanex 302] = 0.05 M, agitation speed = 250 rpm, sample = real photographic waste, and stripping agent = 1.0 M thiourea in 1.0 M H_2SO_4, diluent = kerosene, and [Span 80] (w/v) = (a) 1%, (b) 2%, (c) 3%, (d) 5%, and (e) 7%.

(a) 1% Span 80

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2092.09	2092.09	0.00	1.00
1	2092.09	472.249	77.43	0.23
3	2092.09	113.084	94.59	0.05
5	2092.09	109.143	94.78	0.05
7.5	2092.09	141.567	93.23	0.07
10	2092.09	233.145	88.86	0.11
15	2092.09	300.581	85.63	0.14
20	2092.09	486.278	76.76	0.23

(b) 2 % Span 80

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	3017.143	3017.143	0.00	1.00
1	3017.143	967.91	67.92	0.32
3	3017.143	340.599	88.71	0.11
5	3017.143	68.572	97.73	0.02
7.5	3017.143	76.239	97.47	0.03
10	3017.143	106.524	96.47	0.04
15	3017.143	125.624	95.84	0.04
20	3017.143	171.774	94.31	0.06

(c) 3% Span 80

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	3177.28	3177.28	0.00	1.00
1	3177.28	548.603	82.73	0.17
3	3177.28	137.089	95.69	0.04
5	3177.28	107.187	96.63	0.03
7.5	3177.28	109.359	96.56	0.03
10	3177.28	157.067	95.06	0.05
15	3177.28	129.472	95.93	0.04
20	3177.28	289.294	90.89	0.09

(d) 5 % Span 80

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1.00
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.29	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.02
20	2054.561	116.826	94.31	0.06

(e) 7 % Span 80

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2805.177	2805.177	0.00	1.00
1	2805.177	1064.185	62.06	0.38
3	2805.177	355.244	87.34	0.13
5	2805.177	133.101	95.26	0.05
7.5	2805.177	112.939	95.97	0.04
10	2805.177	126.784	95.48	0.05
15	2805.177	238.798	91.49	0.09
20	2805.177	251.257	91.04	0.09

Table B7: Data of effect of treat ratio (Experimental conditions: [Cyanex 302] = 0.05 M, agitation speed = 250 rpm, sample = real photographic waste, and strip agent = 1.0 M thiourea in 1.0 M H_2SO_4, diluent = kerosene, [Span 80] = 5% (w/v), and treat ratio = (a) 1:3, (b) 1:5, (c) 1:6, and (d) 1:7.

(a) TR 1: 3

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2156.932	2156.932	0.00	1.00
1	2156.932	93.974	95.64	0.04
3	2156.932	13.966	99.35	0.01
5	2156.932	8.818	99.59	0.00
7.5	2156.932	8.709	99.60	0.00
10	2156.932	8.509	99.61	0.00
15	2156.932	14.284	99.34	0.01
20	2156.932	36.434	98.31	0.02

(b) TR 1:5

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1.00
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.29	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.02
20	2054.561	116.826	94.31	0.06

(c) TR 1:6

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2259.2	2259.2	0.00	1.00
1	2259.2	1120	50.42	0.50
3	2259.2	831.4	63.20	0.37
5	2259.2	851.8	62.30	0.38
7.5	2259.2	927	58.97	0.41
10	2259.2	1123.4	50.27	0.50
15	2259.2	1277.8	43.44	0.57
20	2259.2	1360.2	39.79	0.60

(d) TR 1:7

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2470.368	2470.368	0.00	1.00
1	2470.368	1479.993	40.09	0.60
3	2470.368	995.284	59.71	0.40
6	2470.368	1235.031	50.01	0.50
8	2470.368	1386.206	43.89	0.56
10	2470.368	1451.017	41.26	0.59
15	2470.368	1580.237	36.03	0.64
20	2470.368	1744.676	29.38	0.71

Table B8: Data of effect of agitation speed (Experimental conditions: [Cyanex 302] = 0.05 M, sample = real photographic waste, and stripping agent = 1.0 M thiourea in 1.0 M H_2SO_4, diluent = kerosene, [Span 80] = 5% (w/v), treat ratio = 1:5, and agitation speed= (a) 200 rpm, (b) 250 rpm, (c) 300 rpm, and (d) 350 rpm.

(a) 200 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2711.797	2711.797	0.00	1.00
1	2711.797	1401.055	48.33	0.52
3	2711.797	927.197	65.81	0.34
5	2711.797	461.264	83.00	0.17
7.5	2711.797	437.522	83.87	0.16
10	2711.797	258.239	90.48	0.10
15	2711.797	165.865	93.88	0.06
20	2711.797	180.495	93.34	0.07

(b) 250 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1.00
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.29	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.02
20	2054.561	116.826	94.31	0.06

(c) 300 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	1677.844	1677.844	0.00	1.00
1	1677.844	457.727	72.72	0.27
3	1677.844	97.089	94.21	0.06
5	1677.844	101.915	93.93	0.06
7.5	1677.844	132.842	92.08	0.08
10	1677.844	167.103	90.04	0.10
15	1677.844	197.114	88.25	0.12
20	1677.844	362.849	78.37	0.22

(d) 350 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	871.577	871.577	0.00	1.00
1	871.577	178.488	79.52	0.20
3	871.577	66.354	92.39	0.08
5	871.577	80.562	90.76	0.09
7.5	871.577	91.662	89.48	0.11
10	871.577	85.832	90.15	0.10
15	871.577	187.411	78.50	0.22
20	871.577	144.042	83.47	0.17

Table B9: Data of effect of homogenizer speed (Experimental conditions: [Cyanex 302] = 0.05 M, sample = real photographic waste, and strip agent = 1.0 M thiourea in 1.0 M H_2SO_4, diluents = kerosene, [Span 80] = 5% (w/v), treat ratio = 1:5, agitation speed= 250 rpm, and homogenizer Speed= (a) 8000 rpm, (b) 9500 rpm, (c) 13500 rpm.

(a) 8000 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2763.73	2763.73	0.00	1.00
1	2763.73	1343.869	51.37	0.49
3	2763.73	770.507	72.12	0.28
5	2763.73	487.658	82.36	0.18
10	2763.73	357.135	87.08	0.13
15	2763.73	623.484	77.44	0.23
20	2763.73	636.986	76.95	0.23

(b) 9500 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2707.264	2707.264	0.00	1.00
1	2707.264	835.171	69.15	0.31
3	2707.264	586.17	78.35	0.22
5	2707.264	276.497	89.79	0.10
7.5	2707.264	244.362	90.97	0.09
10	2707.264	248.488	90.82	0.09
15	2707.264	278.179	89.72	0.10
20	2707.264	388.282	85.66	0.14

(c) 13500 rpm

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.561	2054.561	0.00	1.00
1	2054.561	300.485	85.37	0.15
3	2054.561	33.959	98.35	0.02
5	1968.275	41.539	97.89	0.02
7.5	2010.316	34.45	98.29	0.02
10	1968.275	50.698	97.42	0.03
15	1968.275	38.449	98.05	0.02
20	2054.561	116.826	94.31	0.06

Table B10: Data of metal selectivity (Experimental conditions: [Cyanex 302] = 0.05 M, sample = real photographic waste, and stripping agent = 1.0 M thiourea in 1.0 M H_2SO_4, diluents = kerosene, [Span 80] = 5% (w/v), treat ratio = 1:5, and agitation speed= 250 rpm)

(a) Silver (Ag)

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	2054.56	2054.56	0.00	1.00
1	2054.56	300.485	85.37	0.15
3	2054.56	33.959	98.35	0.02
5	1968.28	41.539	97.89	0.02
7.5	2010.32	34.45	98.27	0.02
10	1968.28	50.698	97.42	0.03
15	1968.28	38.449	98.05	0.02
20	2054.56	116.826	94.31	0.06

(b) Pottassium (K)

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	8037.22	8037.22	0.00	1.00
1	8037.22	7028.33	12.55	0.87
3	8037.22	7097	11.70	0.88
5	6893.27	6804.85	1.28	0.99
7.5	6893.27	6810	1.21	0.99
10	6893.27	6585.6	4.46	0.96
15	6893.27	6382.1	7.42	0.93
20	8037.22	6180.83	23.10	0.77

(c) Sodium (Na)

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	3090.64	2701.31	0.00	1.00
1	3090.64	2699.81	12.59	0.87
3	3232.17	3179.89	12.65	0.87
5	3232.17	3100	1.62	0.98
7.5	3232.17	3086.3	4.09	0.96
10	3232.17	2774.31	4.51	0.95
15	3090.64	2471.6	14.17	0.86
20	3090.64	2701.31	20.03	0.80

(d) Ferum (Fe)

Time	Original (ppm)	Aqueous (ppm)	% extracted	Ce/Co
0	1421.4	1421.4	0.00	1.00
1	1421.4	1419.5	0.13	1.00
3	1421.4	1317.12	7.34	0.93
5	2002.15	1983.99	0.91	0.99
7.5	2002.15	1910	4.60	0.95
10	2002.15	1884.7	5.87	0.94
15	2002.15	1834.22	8.39	0.92
20	1421.4	1331.19	6.35	0.94

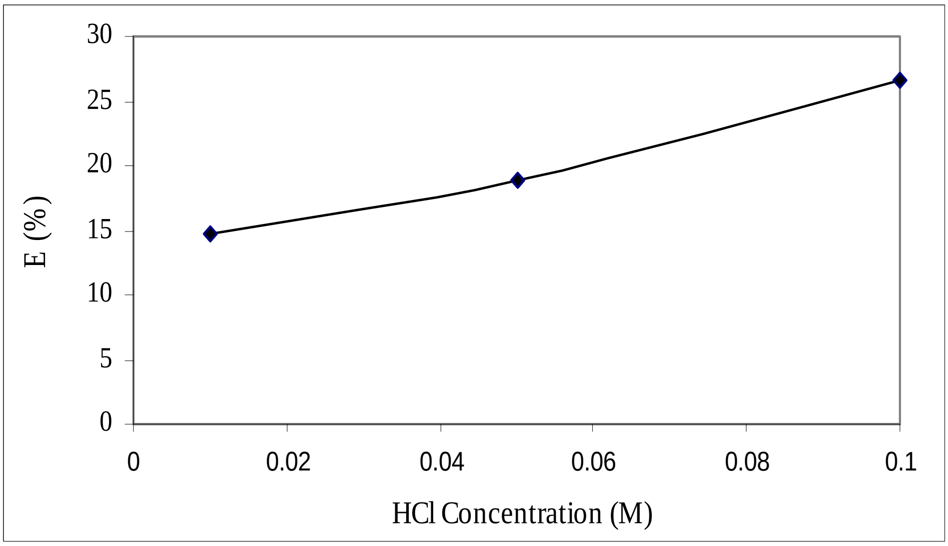


Figure B1: Effect of HCl concentration in the stripping agent on the extraction of silver ([TMTDS] = 0.03 M in toluene, residence time = 6 min, Span 80 = 5% w/v, agitation speed = 250 rpm, treat ratio = 1:5)

APPENDIX C

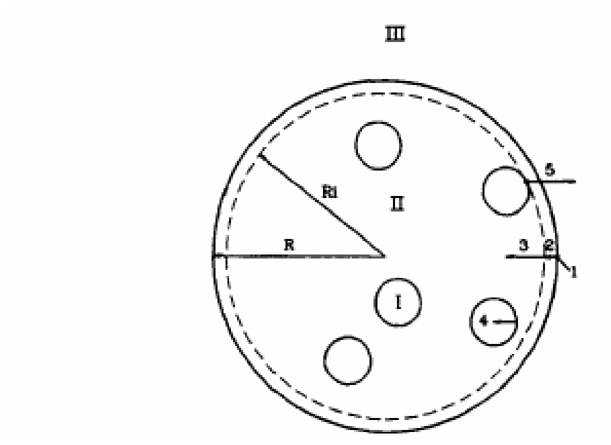
EFFECTIVE DIFFUSIVITY

In a emulsion liquid membrane (ELM) operation, a solute is transferred through the organic membrane from the external continuous phase to the internal droplet phase, where the solute transfer macroscopically proceeds from the external phase toward the

center of the (W/O) emulsion drop containing numbers of internal aqueous droplets. To elucidate the mechanism of the LSM permeation, the analysis of diffusion process within the emulsion drop is crucial; in particular, effective diffusivity of solute in a (W/O) emulsion drop is one of the important parameters for modeling the permeation of the solute through ELMs. Several expressions for evaluating the effective diffusivity have been proposed (Ho and Li, 1992); however, the validity of the models has been examined indirectly from the time course of solute concentration in the continuous aqueous phase in stirred batch vessel. For the elucidation of permeation mechanism, a column operation is favorable rather than stirred vessel operation from the points of view of both residences time distribution and stability of (W/O) emulsion drops.

In the immobilized globule model, being one of geometric models for (W/O) emulsion drops, the internal aqueous droplets are assumed to be distributed uniformly in the drop and not to be mixed with each other. Thus, it provides an improvement over the other models since no curve fitting is required for the parameter estimation. When a reaction advances deep inside the drop, however, it might give an unfavorable prediction (Chan and Lee, 1984).

There are some models for evaluating effective diffusivity in (W/O) emulsion drops; however, the models have not taken mass-transfer resistance through the interface between the internal aqueous and membrane phases into consideration. Here, a permeation model for (W/O) emulsion drop will be presented by extending the cubic model derived by Teramoto and Matsuyama (1986). Figure C1 shows the schematic diagram of a constitution element of (W/O) emulsion phase, whose large cube consists of a small cube as an internal aqueous droplet and an annular cube as the membrane phase surrounding the droplet. Assuming that a (W/O) emulsion drop consists of a large number of such elements and the permeation of solute in the drop takes place only in the direction of the radius, we can consider that the permeation process proceeds in parallel through the elements of the organic membrane liquid and the aqueous droplet. In Figure C1 the volume of the small cube and its volume fraction to the element are equal to the volume of an internal droplet having d_i in diameter and the volume fraction of the internal aqueous phase in the emulsion phase, ϕ.



1. Extraction reaction at the external interface
2. Diffusion in thin oil layer
3. Diffusion in W/O emulsion phase
4. Stripping reaction at internal interface
5. Leakage of the internal phase to the external phase

Figure C1: Permeation model of metal ion by an emulsion liquid membrane (Lee et al., 1996).

In this study, the effective diffusivity of the complex, D_{ex}, was derived to modify Teramoto et al.'s model. The model is schematically shown in Figure C2. A small cube represents an internal droplet, and a larger cube represents an element consisting of an internal droplet and an organic membrane solution surrounding the droplet. The fluxes through paths 1, 2 and 3 can be calculated in this model, and given by Equations C1-C3, respectively.

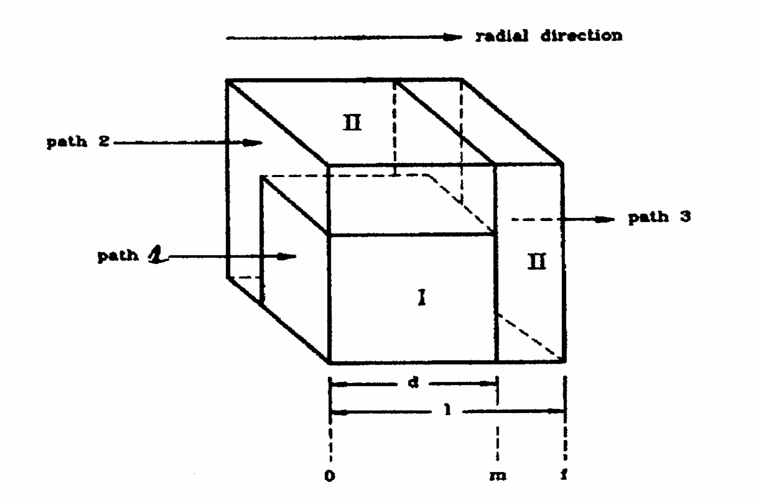


Figure C2: A cube represents an emulsion globuled

$$J_1 = k_s C_{xo} C_{Ho} \tag{C1}$$

$$J_2 = \frac{D_c}{d}\left(C_{xo} C_{Cm}\right) \tag{C2}$$

$$J_3 = \frac{D_c}{1-d}\left(C_{Cm} - C_{Cf}\right) \tag{C3}$$

Where the subscripts, o, m and f, represent the position in the model of Figure C2. Initially, C_{co} : ~ C_{cm} , and the contribution of J_1 on total mass transfer decreases rapidly with time. Also, C_{Ho} in Equation D1 is equal to C_H, average hydrogen ion concentration in a small cube, because the size of internal droplet is very small. So, J_l can be written as follows:

$$J_1 = k_s C_H \left(C_{Co} - C_{Cm}\right) \tag{C4}$$

D_c is the lumped parameter for the diffusivity of the silver-carrier complex in the membrane phase. This involves the circulating effect of the internal aqueous droplets inside the emulsion drop. In reality, at low surfactant concentration like in the present experimental conditions, the internal aqueous droplets are mobile to some degree inside the emulsion drop because of the low viscosity of the membrane phase. Such mobility

corresponds to the increase in the diffusion rate of the complex in the membrane phase. From the model, the continuity of silver complex at steady state is expressed by

$$l^2 J = d^2 J_1 + \left(l^2 - d^2\right) J_2 = l^2 J_3 \tag{C5}$$

and the effective diffusivity is defined by

$$J = D_{eC}\frac{\partial C_C}{\partial r} = \frac{D_{eC}}{l}\left(C_{Co} - C_{Cf}\right) \tag{C6}$$

From Equations C2-C5, the flux of the complex is obtained:

$$J = \frac{\left(C_{Co} - C_{Cf}\right)/l}{\dfrac{1}{D_C\left(\phi^{-1/3} - \phi^{1/3}\right) + k_s C_H \phi^{1/3}\left(\frac{4}{3}\pi R_\mu{}^3\right)^{1/3}} + \dfrac{1-\phi^{1/3}}{D_C}} \tag{C7}$$

where ϕ is the volume fraction of internal aqueous phase in an emulsion drop. Finally, the reciprocal of the denominator of Equation C7 corresponds to D_{eC}.

$$D_{eC} = D_C\left[\frac{1}{\phi^{-1/3} - \phi^{1/3} + \dfrac{k_s C_H}{D_C}\phi^{1/3}\left(\frac{4}{3}\pi R_\mu{}^3\right)^{1/3}} + 1 - \phi^{1/3}\right]^{-1} \tag{C8}$$

The stripping reaction rate constant, ks, were determined by optimization to obtain a minimum difference between the calculated results and the experimental data. D_B was assumed to be equal to Dc because the molecular diffusivity of silver complex was almost equal to that of carrier.

C.1 Solute Diffusivity in Membrane Phase

The diffusivity of silver –Cyanex 302 complex in the membrane phase as evaluated by the Wilke-Chang equation;

The Wilke-Chang equation is:

$$D_C = 7.4x10^{-12} (\phi M_B)^{0.5} T / \mu_B V_c{}^{0.6}) \text{ m}^2\text{/s}$$

Where, μ_B is the viscosity of the organic membrane phase, and Vc is the molar volume of the solute-extractant complex at its normal boiling point. The viscosity was obtained from experiments. The organic membrane solution is made in the same composition like in the emulsion liquid membrane extraction. Molar volume is difficult to obtain from the experiments because of our limited equipment. Because this emulsion liquid membrane system was invented by us, the properties of solute-extractant complex also are difficult to obtain from literature. Some correlations are recommended for the use to calculate Vc. Schroedor (Reid, 1977) has suggested a novel and simple additive method with small errors for estimating molar volumes at the normal boiling point. Their rule is to count the numbers of atoms of carbon, hydrogen, oxygen and nitrogen, add one for each double bond and multiply the sum by seven. This gives the molar volume of silver-Cyanex 302 complex is (1.3538 x 7) cm^3/mol.

D.2 Mass Transfer Coefficient

The thickness, δ of the thin oil layer is considered to be equivalent to the thickness $l - d$ of the oil membrane phase surrounding the internal aqueous droplet, and is expressed by

$$\delta = l - d = (4\pi / 3)^{1/3} R_\mu (\phi^{-1/3} - 1) \qquad \text{(C9)}$$

Hence, the mass transfer coefficient k_c and k_B in the thin oil layer are given by

$$k_C = \frac{D_C}{\delta}, k_B = \frac{D_B}{\delta} = 0.0022 \qquad \text{(C10)}$$

APPENDIX D

SAUTER MEAN DIAMETER

In emulsion liquid membrane extraction, the emulsions are dispersed in the external aqueous phase by agitation to disperse heterogeneous phases. A size distribution of the emulsion globules is formed with mixing. The size distribution of these emulsion globules depends on the mixer and the properties of emulsion. Many trial, which include different compositions of the emulsion and mixing speeds are required to find the size of emulsion droplets and globules at optimum condition of emulsion liquid membrane system. However, only a few pictures were satisfy to analyze using image analyzer.

The Sauter mean diameter is defined as follows:

$$D_{32} = \left(3\sum D_p^3\right)/\left(3\sum D_p^2\right) \tag{D1}$$

where D_p is the diameter of each droplet. When the emulsion liquid membrane is in the extractor, the size of the emulsion globules in the extractor can be obtained by photography. Then, Sauter mean diameter is calculated by its definition. The size of emulsion globules at 250 rpm is 0.5 mm. However, for other speed the Reis and Carvalho (2004) correlation was used to predict the size of emulsion globules.

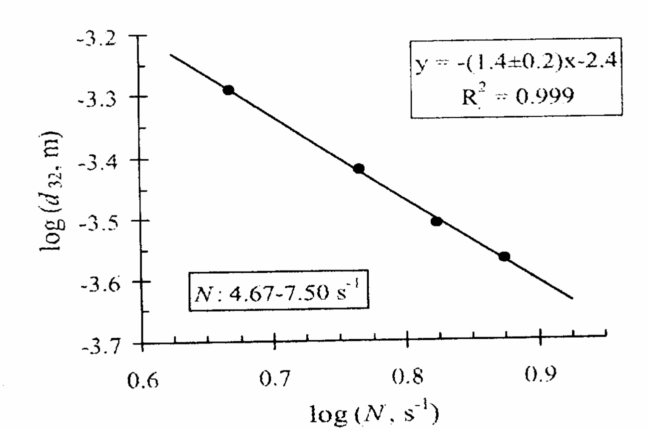


Figure D1: Effect of stirring speed on the sauter mean diameter of the emulsion globules (Reis and Carvalho, 2004)

For determining the size of emulsion droplet of W/O emulsion, the procedures is followed.

Reagents:

Membrane phase: Kerosene with 0.05 M Cyanex 302 and 5% w/v Span 80

Stripping phase: 1 M thiourea in 1 M H_2SO_4

The emulsion was made similarly to the previous methods. A Stereo-microscope with colour camera was used to snap emulsion picture with is direct connected to computer. Because of emulsion droplet are very small, it is difficult to directly observe the droplet sizes. A few repeating step should be done until a clearly emulsion picture observed in the computer monitor.

A small scale was also recorded in the microscope focus area. For obtaining more exact result, the caption picture was analyzed with image analyzer. Table D1 shows the size of emulsion droplets after 5 minutes time homogenizing. Around 200 of clear droplets were calculated according to Equation D1. The sauter mean diameter of emulsion droplets found for this study is 3.31μm.

Table D1: Size of emulsion droplets at different homogenizer speed.

Homogenizer speed							
13500 rpm				8000rpm			
radious (micron)	diameter (micron)	Dp^3	Dp^2	radious (micron)	diameter (micron)	Dp^3	Dp^2
4.727	9.454	844.9807	89.378116	7.838	15.676	3852.173	245.737
3.95	7.9	493.039	62.41	9.089	18.178	6006.733	330.4397
4.9135	9.827	948.9927	96.569929	6.161	12.322	1870.87	151.8317
4.693	9.386	826.8784	88.096996	9.354	18.708	6547.599	349.9893
4.3875	8.775	675.6805	77.000625	9.461	18.922	6774.872	358.0421
4.9335	9.867	960.6283	97.357689	8.554	17.108	5007.232	292.6837
4.0425	8.085	528.494	65.367225	8.544	17.088	4989.692	291.9997
5.446	10.892	1292.18	118.63566	6.981	13.962	2721.717	194.9374
4.0065	8.013	514.5001	64.208169	6.583	13.166	2282.241	173.3436
4.9945	9.989	996.7036	99.780121	6.379	12.758	2076.576	162.7666
4.312	8.624	641.396	74.373376	7.145	14.29	2918.077	204.2041
5.2945	10.589	1187.312	112.12692	8.098	16.196	4248.379	262.3104
2.5835	5.167	137.948	26.697889	7.097	14.194	2859.66	201.4696
3.8665	7.733	462.4279	59.799289	7.687	15.374	3633.797	236.3599
4.476	8.952	717.3981	80.138304	6.882	13.764	2607.558	189.4477
5.446	10.892	1292.18	118.63566	9.087	18.174	6002.768	330.2943
4.546	9.092	751.5853	82.664464	6.489	12.978	2185.865	168.4285
4.635	9.27	796.598	85.9329	6.25	12.5	1953.125	156.25
4.9335	9.867	960.6283	97.357689	7.339	14.678	3162.282	215.4437
4.2185	8.437	600.5707	71.182969	6.513	13.026	2210.208	169.6767
4.3135	8.627	642.0656	74.425129	2.639	5.278	147.0307	27.85728
4.7665	9.533	866.3408	90.878089	7.509	15.018	3387.165	225.5403
3.748	7.496	421.2004	56.190016	5.883	11.766	1628.87	138.4388
3.6365	7.273	384.7165	52.896529	6.578	13.156	2277.045	173.0803
3.949	7.898	492.6646	62.378404	7.014	14.028	2760.497	196.7848
4.614	9.228	785.8194	85.155984	8.028	16.056	4139.159	257.7951
4.412	8.824	687.0629	77.862976	5.804	11.608	1564.128	134.7457
4.2185	8.437	600.5707	71.182969	7.276	14.552	3081.542	211.7607
2.5835	5.167	137.948	26.697889	5.622	11.244	1421.551	126.4275
3.6315	7.263	383.1317	52.751169	7.862	15.724	3887.667	247.2442
4.3825	8.765	673.3731	76.825225	9.103	18.206	6034.532	331.4584
4.095	8.19	549.3533	67.0761	9.193	18.386	6215.295	338.045
4.9335	9.867	960.6283	97.357689	6.801	13.602	2516.566	185.0144
4.7775	9.555	872.3526	91.298025	7.761	15.522	3739.754	240.9325
3.569	7.138	363.6886	50.951044	6.558	13.116	2256.338	172.0295
3.6315	7.263	383.1317	52.751169	6.495	12.99	2191.934	168.7401
2.7695	5.539	169.9394	30.680521	3.34	6.68	298.0776	44.6224
2.5635	5.127	134.769	26.286129	6.842	13.684	2562.354	187.2519
3.057	6.114	228.5474	37.380996	9.419	18.838	6685.046	354.8702
4.7215	9.443	842.0347	89.170249	9.146	18.292	6120.453	334.5973
3.355	6.71	302.1117	45.0241	8.05	16.1	4173.281	259.21
2.5635	5.127	134.769	26.286129	7.824	15.648	3831.568	244.8599

Table E1: Continued

Homogenizer speed							
13500 rpm				8000rpm			
radious (micron)	diameter (micron)	Dp^3	Dp^2	radious (micron)	diameter (micron)	Dp^3	Dp^2
2.975	5.95	210.6449	35.4025	7.509	15.018	3387.165	225.5403
2.389	4.778	109.0783	22.829284	7.929	15.858	3987.909	251.4762
3.202	6.404	262.6358	41.011216	8.071	16.142	4206.027	260.5642
2.5835	5.167	137.948	26.697889	9.879	19.758	7713.1	390.3786
3.057	6.114	228.5474	37.380996	8.227	16.454	4454.659	270.7341
2.2905	4.581	96.13485	20.985561	10.4	20.8	8998.912	432.64
2.4815	4.963	122.2455	24.631369	8.774	17.548	5403.596	307.9323
2.193	4.386	84.37346	19.236996	9.249	18.498	6329.572	342.176
3.057	6.114	228.5474	37.380996	8.616	17.232	5116.902	296.9418
4.0135	8.027	517.2015	64.432729	6.292	12.584	1992.765	158.3571
2.9925	5.985	214.384	35.820225	8.133	16.266	4303.703	264.5828
3.4095	6.819	317.0751	46.498761	7.798	15.596	3793.496	243.2352
3.1845	6.369	258.3531	40.564161	8.916	17.832	5670.223	317.9802
2.2925	4.585	96.3869	21.022225	7.608	15.216	3522.91	231.5267
2.7695	5.539	169.9394	30.680521	7.171	14.342	2950.048	205.693
2.1365	4.273	78.01869	18.258529	7.827	15.654	3835.977	245.0477
2.6805	5.361	154.0769	28.740321	6.976	13.952	2715.873	194.6583
2.6125	5.225	142.6458	27.300625	5.469	10.938	1308.621	119.6398
2.35	4.7	103.823	22.09	7.509	15.018	3387.165	225.5403
2.0865	4.173	72.66833	17.413929	3.886	7.772	469.4598	60.40398
1.9235	3.847	56.93333	14.799409	4.843	9.686	908.7269	93.8186
2.5835	5.167	137.948	26.697889	3.792	7.584	436.2094	57.51706
2.2905	4.581	96.13485	20.985561	2.826	5.652	180.5537	31.9451
2.6935	5.387	156.3295	29.019769	3.064	6.128	230.121	37.55238
2.2925	4.585	96.3869	21.022225	3.257	6.514	276.4033	42.4322
2.35	4.7	103.823	22.09	5.18	10.36	1111.935	107.3296
2.5835	5.167	137.948	26.697889	4.279	8.558	626.7825	73.23936
2.193	4.386	84.37346	19.236996	4.864	9.728	920.5994	94.63398
2.193	4.386	84.37346	19.236996	6.242	12.484	1945.635	155.8503
2.044	4.088	68.31761	16.711744	4.4	8.8	681.472	77.44
2.086	4.172	72.6161	17.405584	4.642	9.284	800.2126	86.19266
2.2925	4.585	96.3869	21.022225	5.707	11.414	1487.009	130.2794
2.1365	4.273	78.01869	18.258529	3.217	6.434	266.3442	41.39636
2.2905	4.581	96.13485	20.985561	4.707	9.414	834.3006	88.6234
2.5175	5.035	127.6434	25.351225	3.059	6.118	228.9963	37.42992
3.714	7.428	409.8413	55.175184	3.732	7.464	415.8291	55.7113
2.6805	5.361	154.0769	28.740321	3.785	7.57	433.7981	57.3049
2.5835	5.167	137.948	26.697889	2.222	4.444	87.76516	19.74914
2.9085	5.817	196.8327	33.837489	4.139	8.278	567.2523	68.52528
2.5835	5.167	137.948	26.697889	0	0	0	0
2.3285	4.657	100.9994	21.687649	2.972	5.944	210.0083	35.33114
2.2555	4.511	91.79488	20.349121	7.257	14.514	3057.464	210.6562
2.086	4.172	72.6161	17.405584	5.325	10.65	1207.95	113.4225

Table E1: Continued

Homogenizer speed							
13500 rpm				8000rpm			
radious (micron)	diameter (micron)	Dp^3	Dp^2	radious (micron)	diameter (micron)	Dp^3	Dp^2
.6785	3.357	37.83154	11.269449	2.818	5.636	179.0247	31.7645
2.044	4.088	68.31761	16.711744	7.536	15.072	3423.834	227.1652
1.1735	2.347	12.92824	5.508409	6.928	13.856	2660.196	191.9887
2.0115	4.023	65.11036	16.184529	8.337	16.674	4635.743	278.0223
2.3285	4.657	100.9994	21.687649	8.183	16.366	4383.567	267.846
1.7625	3.525	43.80033	12.425625	9.08	18.16	5988.906	329.7856
2.0115	4.023	65.11036	16.184529	7.887	15.774	3924.872	248.8191
2.3885	4.777	109.0098	22.819729	7.701	15.402	3653.687	237.2216
2.35	4.7	103.823	22.09	2.066	4.132	70.54739	17.07342
2.2925	4.585	96.3869	21.022225	3.525	7.05	350.4026	49.7025
2.35	4.7	103.823	22.09	2.63	5.26	145.5316	27.6676
1.998	3.996	63.80819	15.968016	3.269	6.538	279.4697	42.74544
2.3885	4.777	109.0098	22.819729	3.355	6.71	302.1117	45.0241
2.35	4.7	103.823	22.09	6.839	13.678	2558.985	187.0877
2.3285	4.657	100.9994	21.687649	8.573	17.146	5040.672	293.9853
1.998	3.996	63.80819	15.968016	9.371	18.742	6583.363	351.2626
2.193	4.386	84.37346	19.236996	8.846	17.692	5537.717	313.0069
2.193	4.386	84.37346	19.236996	11.682	23.364	12753.86	545.8765
2.6125	5.225	142.6458	27.300625	10.261	20.522	8642.891	421.1525
2.0115	4.023	65.11036	16.184529	9.028	18.056	5886.602	326.0191
1.6785	3.357	37.83154	11.269449	8.913	17.826	5664.502	317.7663
1.7625	3.525	43.80033	12.425625	13.594	27.188	20097.03	739.1873
1.9235	3.847	56.93333	14.799409	8.178	16.356	4375.536	267.5187
1.487	2.974	26.30407	8.844676	9.011	18.022	5853.41	324.7925
1.709	3.418	39.93155	11.682724	11.029	22.058	10732.44	486.5554
1.6555	3.311	36.29757	10.962721	8.215	16.43	4435.195	269.9449
1.405	2.81	22.18804	7.8961	8.931	17.862	5698.89	319.051
1.6785	3.357	37.83154	11.269449	9.021	18.042	5872.919	325.5138
1.299	2.598	17.53547	6.749604	9.38	18.76	6602.349	351.9376
1.588	3.176	32.03624	10.086976	8.096	16.192	4245.233	262.1809
1.6785	3.357	37.83154	11.269449	8.467	16.934	4856	286.7604
1.588	3.176	32.03624	10.086976	6.684	13.368	2388.907	178.7034
1.836	3.672	49.51172	13.483584	8.05	16.1	4173.281	259.21
2.3885	4.777	109.0098	22.819729	9.407	18.814	6659.528	353.9666
2.35	4.7	103.823	22.09	4.513	9.026	735.3363	81.46868
1.405	2.81	22.18804	7.8961	5.289	10.578	1183.616	111.8941
1.6265	3.253	34.42328	10.582009	4.485	8.97	721.7343	80.4609
1.588	3.176	32.03624	10.086976	3.306	6.612	289.067	43.71854
1.405	2.81	22.18804	7.8961	3.788	7.576	434.8304	57.39578
3.4095	6.819	317.0751	46.498761	4.981	9.962	988.6433	99.24144
2.3805	4.761	107.9182	22.667121	5.17	10.34	1105.507	106.9156
3.409	6.818	316.9356	46.485124	3.284	6.568	283.3345	43.13862
3.2895	6.579	284.7604	43.283241	3.5	7	343	49

Table E1: Continued

Homogenizer speed							
13500 rpm				8000rpm			
radious (micron)	diameter (micron)	Dp^3	Dp^2	radious (micron)	diameter (micron)	Dp^3	Dp^2
2.7945	5.589	174.5832	31.236921	4.123	8.246	560.6993	67.99652
2.6935	5.387	156.3295	29.019769	4.455	8.91	707.348	79.3881
2.9085	5.817	196.8327	33.837489	3.516	7.032	347.7255	49.44902
2.6935	5.387	156.3295	29.019769	3.451	6.902	328.7947	47.6376
2.6935	5.387	156.3295	29.019769	3.672	7.344	396.0938	53.93434
2.5635	5.127	134.769	26.286129	3.943	7.886	490.4224	62.189
2.777	5.554	171.3238	30.846916	4.006	8.012	514.3075	64.19214
1.6785	3.357	37.83154	11.269449	4.75	9.5	857.375	90.25
2.1095	4.219	75.09804	17.799961	4.216	8.432	599.5036	71.09862
2.4815	4.963	122.2455	24.631369	4.539	9.078	748.1187	82.41008
2.012	4.024	65.15893	16.192576	4.015	8.03	517.7816	64.4809
2.3935	4.787	109.6959	22.915369	3.825	7.65	447.6971	58.5225
2.3885	4.777	109.0098	22.819729	3.642	7.284	386.4647	53.05666
2.193	4.386	84.37346	19.236996	3.426	6.852	321.7007	46.9499
1.9235	3.847	56.93333	14.799409	4.054	8.108	533.0172	65.73966
2.5905	5.181	139.0723	26.842761	4.095	8.19	549.3533	67.0761
1.8135	3.627	47.71365	13.155129	6.802	13.604	2517.676	185.0688
1.63	3.26	34.64598	10.6276	3.758	7.516	424.5808	56.49026
1.7625	3.525	43.80033	12.425625	4.912	9.824	948.1238	96.51098
2.086	4.172	72.6161	17.405584	4.053	8.106	532.6229	65.70724
1.9235	3.847	56.93333	14.799409	3.937	7.874	488.187	61.99988
1.998	3.996	63.80819	15.968016	5.072	10.144	1043.825	102.9007
1.836	3.672	49.51172	13.483584	6.606	13.212	2306.246	174.5569
1.6785	3.357	37.83154	11.269449	7.191	14.382	2974.801	206.8419
2.35	4.7	103.823	22.09	6.833	13.666	2552.256	186.7596
1.9235	3.847	56.93333	14.799409	5.242	10.484	1152.341	109.9143
2.044	4.088	68.31761	16.711744	3.88	7.76	467.2886	60.2176
2.044	4.088	68.31761	16.711744	4.016	8.032	518.1686	64.51302
2.086	4.172	72.6161	17.405584	3.464	6.928	332.5245	47.99718
1.9235	3.847	56.93333	14.799409	3.216	6.432	266.0959	41.37062
1.9235	3.847	56.93333	14.799409	1.95	3.9	59.319	15.21
2.0015	4.003	64.14411	16.024009	2.186	4.372	83.56809	19.11438
2.086	4.172	72.6161	17.405584	4.018	8.036	518.9432	64.5773
2.3805	4.761	107.9182	22.667121	6.409	12.818	2106.012	164.3011
2.5835	5.167	137.948	26.697889	5.742	11.484	1514.536	131.8823
2.3285	4.657	100.9994	21.687649	6.212	12.424	1917.716	154.3558
2.5175	5.035	127.6434	25.351225	6.09	12.18	1806.932	148.3524
2.1365	4.273	78.01869	18.258529	6.933	13.866	2665.96	192.266
2.458	4.916	118.8052	24.167056	5.778	11.556	1543.201	133.5411
2.2905	4.581	96.13485	20.985561	6.711	13.422	2417.974	180.1501
2.3285	4.657	100.9994	21.687649	7.259	14.518	3059.993	210.7723
2.35	4.7	103.823	22.09	3.383	6.766	309.7391	45.77876
2.086	4.172	72.6161	17.405584	3.137	6.274	246.9639	39.36308

Table E1: Continued

Homogenizer speed							
13500 rpm				8000rpm			
radious (micron)	diameter (micron)	Dp^3	Dp^2	radious (micron)	diameter (micron)	Dp^3	Dp^2
2.458	4.916	118.8052	24.167056	4.495	8.99	726.5727	80.8201
2.545	5.09	131.8722	25.9081	4.511	9.022	734.3591	81.39648
2.3085	4.617	98.41915	21.316689	4.181	8.362	584.6965	69.92304
2.4815	4.963	122.2455	24.631369	4.275	8.55	625.0264	73.1025
2.5905	5.181	139.0723	26.842761	4.387	8.774	675.4495	76.98308
2.389	4.778	109.0783	22.829284	4.523	9.046	740.2352	81.83012
2.193	4.386	84.37346	19.236996	4.465	8.93	712.122	79.7449
2.35	4.7	103.823	22.09	3.469	6.938	333.9665	48.13584
1.405	2.81	22.18804	7.8961	3.814	7.628	443.8457	58.18638
1.393	2.786	21.62436	7.761796	4.489	8.978	723.6671	80.60448
1.487	2.974	26.30407	8.844676	3.475	6.95	335.7024	48.3025
2.2555	4.511	91.79488	20.349121	3.433	6.866	323.6767	47.14196
1.998	3.996	63.80819	15.968016	2.741	5.482	164.7468	30.05232
2.2905	4.581	96.13485	20.985561	3.45	6.9	328.509	47.61
2.1365	4.273	78.01869	18.258529	2.701	5.402	157.639	29.1816
2.086	4.172	72.6161	17.405584	2.845	5.69	184.22	32.3761
1.836	3.672	49.51172	13.483584	4.551	9.102	754.068	82.8464
1.7625	3.525	43.80033	12.425625	4.292	8.584	632.5125	73.68506
1.405	2.81	22.18804	7.8961	4.693	9.386	826.8784	88.097
2.086	4.172	72.6161	17.405584	3.88	7.76	467.2886	60.2176
2.1095	4.219	75.09804	17.799961	3.992	7.984	508.9341	63.74426
2.012	4.024	65.15893	16.192576	4.715	9.43	838.5618	88.9249
2.4815	4.963	122.2455	24.631369	3.299	6.598	287.2347	43.5336
2.193	4.386	84.37346	19.236996	3.98	7.96	504.3583	63.3616
2.1365	4.273	78.01869	18.258529	4.023	8.046	520.8829	64.73812
2.086	4.172	72.6161	17.405584	3.568	7.136	363.3829	50.9225
1.9235	3.847	56.93333	14.799409	4.65	9.3	804.357	86.49
2.1095	4.219	75.09804	17.799961	4.733	9.466	848.2024	89.60516
2.35	4.7	103.823	22.09	4.409	8.818	685.6623	77.75712
2.044	4.088	68.31761	16.711744	7.373	14.746	3206.437	217.4445
2.012	4.024	65.15893	16.192576	5.792	11.584	1554.446	134.1891
1.588	3.176	32.03624	10.086976	6.343	12.686	2041.616	160.9346
1.998	3.996	63.80819	15.968016	6.378	12.756	2075.599	162.7155
1.836	3.672	49.51172	13.483584	7.192	14.384	2976.042	206.8995
1.8135	3.627	47.71365	13.155129	6.416	12.832	2112.92	164.6602
2.1095	4.219	75.09804	17.799961	6.187	12.374	1894.656	153.1159
1.6555	3.311	36.29757	10.962721	5.965	11.93	1697.936	142.3249
2.1365	4.273	78.01869	18.258529	5.692	11.384	1475.315	129.5955
1.8135	3.627	47.71365	13.155129	6.005	12.01	1732.324	144.2401
2.3885	4.777	109.0098	22.819729	5.216	10.432	1135.279	108.8266
2.5635	5.127	134.769	26.286129	6.084	12.168	1801.597	148.0602
2.6805	5.361	154.0769	28.740321	4.714	9.428	838.0284	88.88718
2.6935	5.387	156.3295	29.019769	5.214	10.428	1133.974	108.7432

Table E1: Continued

Homogenizer speed							
13500 rpm				8000rpm			
radious (micron)	diameter (micron)	Dp^3	Dp^2	radious (micron)	diameter (micron)	Dp^3	Dp^2
2.5635	5.127	134.769	26.286129	4.996	9.992	997.6019	99.84006
2.193	4.386	84.37346	19.236996	2.978	5.956	211.2828	35.47394
3.1175	6.235	242.387	38.875225	3.581	7.162	367.3694	51.29424
3.2895	6.579	284.7604	43.283241	4.227	8.454	604.2084	71.47012
3.2045	6.409	263.2515	41.075281	4.547	9.094	752.0814	82.70084
2.2925	4.585	96.3869	21.022225	3.493	6.986	340.9461	48.8042
2.2925	4.585	96.3869	21.022225	3.77	7.54	428.6611	56.8516
2.2555	4.511	91.79488	20.349121	4.537	9.074	747.1303	82.33748
2.3885	4.777	109.0098	22.819729	4.433	8.866	696.9204	78.60596
2.3285	4.657	100.9994	21.687649	3.622	7.244	380.1328	52.47554
2.3935	4.787	109.6959	22.915369	3.208	6.416	264.115	41.16506
2.2555	4.511	91.79488	20.349121	6.568	13.136	2266.676	172.5545
		45635.46	6889.4639			512689	34726.34
Sauter mean diameter			6.62 micron				14.76 micron

APPENDIX E

EQUILIBRIUM CONSTANT

It is difficult to find the equilibrium constant for extraction reaction by searching literature. Hence, experiments should be done for obtaining this constant.

The extraction reaction occurring on the surface of the emulsion globules is as follow:

$$Ag(S_2O_3)_2^{3-} + \overline{(RH)}_2 \leftrightarrow \overline{Ag(RH)R} + 2(S_2O_3)^{2-} + H^+$$

Where $\overline{(RH)}_2$ and $\overline{Ag(RH)R}$ represent extractant and solute-extractant complex respectively, and both are them exist in the organic phase.

Material and Experiments

Reagents

Solute : Photographic wastes

Extractant: Cyanex 302

Organic diluents: Kerosene

Experiments:

For obtaining as close an extraction reaction as that in emulsion liquid membrane, the external phase and Cyanex 302 in kerosene are the same as those in emulsion liquid membrane.

Preparation of the solutions:

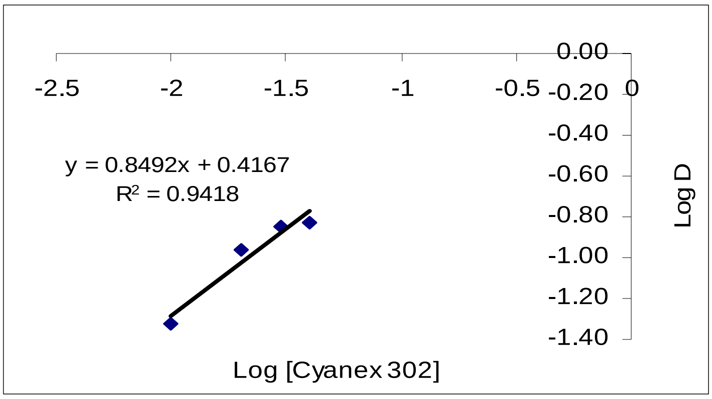
External phase : 100 ml of photographic wastes
Organic phase : 10 ml of kerosene with Cyanex 302.

Experimental Procedures:

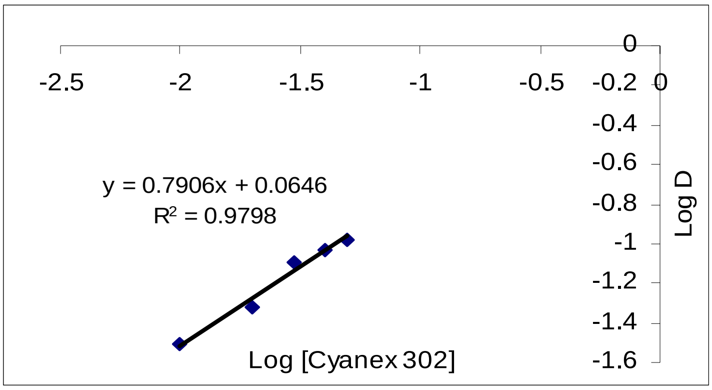
The extraction process will carry out by mixing 100 ml of aqueous and 10 ml of organic solutions (TR= 1:5) using a mechanical shaker which rotation at 250 rpm for a period of one day and then the mixture are carefully pour into separation funnel. Then, after the phase separations achieved (around 15-30 minutes), an aqueous phase will carefully separate from the organic phase. The pH equilibrium is measured. The procedures are repeated for different carrier types. The concentration of silver in the aqueous phase after extraction is measured by AAS. The concentration of silver extracted in organic phase is calculated based on mass balance principle. All experiment will carry out at ambient temperature (26°C).

Results:

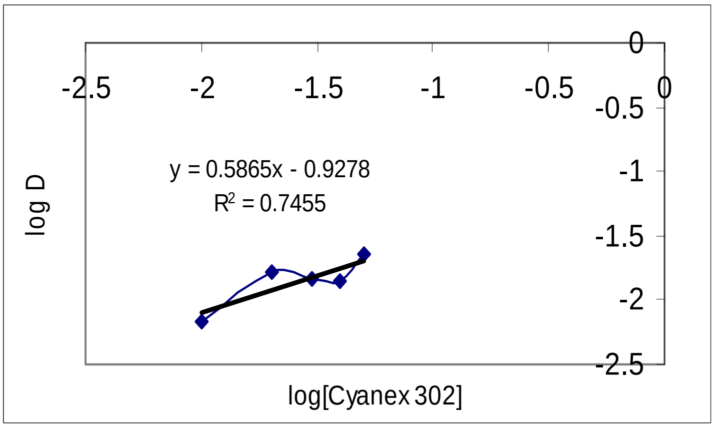
According to extraction reaction, the equilibrium constant can be calculated because the equilibrium concentration of silver and the initial concentration of silver and Cyanex 302 are all known. The equilibrium constant calculated from Figure E1 by considering reaction stoichiometry of extraction reaction is 2.61, 1.16, and 0.118 for treat ratio 1:3, 1:5 and 1:7 respectively.



(a) TR = 1:3



(b) TR = 1:5



(c) TR = 1:7

Figure E1: Determination of Equilibrium Constant for different treat ratio in emulsion liquid membrane

APPENDIX F

PROGRAMMING

F.1 Methods of Solving the ELM Model

The mathematical model of the metal extraction by an emulsion liquid membrane process consists of a combination of parabolic partial differential equations (PDEs), ordinary differential equations (ODEs) and algebraic equations. These equations must be solved simultaneously either using analytical method or numerical method. However, it is very tedious or almost impossible to solve these equations analytically. So, numerical method will be applied to solve these equations. This section is some reviews done on the numerical methods that can be used to solve these equations, especially PDEs and ODEs.

F.1.1 Partial Differential Equations (PDEs)

There are two broad categories of numerical methods that used to solve partial differential equations: (1) finite-difference approaches and (2) finite-element approaches. In the finite-difference methods, the solution domain is divided into a grid of discrete points or nodes. The PDE is then written for each node and its derivatives replaced by finite-divided differences. In contrast to finite-difference techniques, the finite-element method divides the solution domain into simply shaped regions, or “elements”. An approximate solution for the PDE can be developed for each of these elements. The total solution is then generated by linking together, or “assembling” the individual solutions taking care to ensure continuity at the inter-element boundaries. Thus, the PDE is satisfied in a piecewise fashion (Chapra and Canale, 2003).

The finite-difference approaches will be discussed more detail in the following due to its simplicity. There are basically three methods in finite-difference approaches: (1) Explicit methods, (2) Implicit methods and (3) method of lines (Chapra and Canale, 2003).

Reis and Carvalho (2004) used numerical method of lines to solve the partial differential equation system. This technique is based on discretisation of the spatial derivative transforming each partial differential equation into a system of ordinary differential equations (Reis and Carvalho, 2004). A general parabolic partial differential equation is shown in Equation (G.1):

$$\frac{\partial u}{\partial t} = \alpha \frac{\partial^2 u}{\partial x^2} \tag{F1}$$

Constantinides and Mostoufi (1999) showed how to transfer Equation F1 into a set of ordinary differential equations by discretizing only the spatial derivatives using finite differences and leaving the time derivatives unchanged. This concept applied to Equation F1 results in:

$$\frac{du_i}{dt} = \frac{\alpha}{\Delta x^2}\left(u_{i+1} - 2u_i + u_{i-1}\right) \tag{F2}$$

Constantinides and Mostoufi (1999) also stated that there will be as many of these ordinary differential equations as there are grid points in the x-direction. The two equations at the boundaries would have to be modified according to the boundary conditions that are specified in the particular problem (Constantinides and Mostoufi, 1999).

The Equation F2 is the basic for transforming a partial differential equation into a set of ordinary differential equations. However, the partial differential equations in the model are more complex than Equation F1, because they are parabolic equations in three spatial dimensions. Moreover, these parabolic equations involve the circular boundaries. Smith (1974) suggested that finite-difference problems involving circular boundaries can usually be more conveniently in polar coordinates than Cartesian coordinates because they avoid the use of awkward differentiation formulae near the curved boundary. Smith (1974) showed the non-dimensional form of the equation of heat conduction (or diffusion) in three dimensions in spherical polar form:

$$\frac{\partial u}{\partial t} = \nabla^2 u = \frac{\partial^2 u}{\partial r^2} + \frac{2}{r}\frac{\partial u}{\partial r} + \frac{\cot\theta}{r}\frac{\partial u}{\partial \theta} + \frac{1}{r^2}\frac{\partial^2 u}{\partial \theta^2} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 u}{\partial \phi_A^2} \qquad \text{(F3)}$$

If the problem is symmetrical with respect to the origin, it is independent of θ and ϕ_A, so Equation F3 becomes:

$$\frac{\partial u}{\partial t} = \nabla^2 u = \frac{\partial^2 u}{\partial r^2} + \frac{2}{r}\frac{\partial u}{\partial r} \qquad \text{(F4)}$$

with $\partial u / \partial r$ zero at r = 0.

Smith (1974) also showed that at r = 0:

$$\frac{\partial u}{\partial t} = \nabla^2 u = 3\frac{\partial^2 u}{\partial r^2} \qquad \text{(F5)}$$

F.1.2 Ordinary Differential Equations (ODEs)

There are a lot of methods can be used to solve a set of ordinary differential equations (ODEs), for examples, Euler's method, Heun's method, midpoint method and Runge-Kutta (RK) methods (Chapra and Canale, 2003). In general, these methods use numerical method to approximate the slope, then, the slope estimate is used to extrapolate from an old value to a new value.

Since Runge-Kutta (RK) methods are the most popular and accurate methods for solving ordinary differential equations (ODEs), these methods will be discussed in detail. Runge-Kutta (RK) methods achieve the accuracy of a Taylor series approach without requiring the calculation of higher derivatives. Many variations exist but all can be cast in the generalized form of Equation F6 (Chapra and Canale, 2003).

$$y_{i+1} = y_i + g(x_i, y_i, h)h \tag{F6}$$

where $g(x_i, y_i, h)$ is called an increment function, which can be interpreted as a representative slope over the interval. The increment function can be written in general form as: (Chapra and Canale, 2003)

$$g = a_1 k_1 + a_2 k_2 + \ldots + a_n k_n \tag{F7}$$

where the a's are constants and the k's are

$$\begin{aligned}
k_1 &= f(x_i, y_i) \\
k_2 &= f(x_i + p_1 h, y_i + q_{11} k_1 h) \\
k_3 &= f(x_i + p_2 h, y_i + q_{21} k_1 h + q_{22} k_2 h) \\
&\;\;. \\
&\;\;. \\
&\;\;. \\
k_n &= f(x_i + p_{n-1} h, y_i + q_{n-1,1} k_1 h + q_{n-1,2} k_2 h + \ldots + q_{n-1,n-1} k_{n-1} h)
\end{aligned} \tag{F8}$$

where p's and q's are constants. Notice that the k's are recurrence relationships. That is, k_1 appears in the equation for k_2, which appears in the equation for k_3, and so forth. Because each k is a functional evaluation, this recurrence makes RK methods efficient for computer calculations. (Chapra and Canale, 2003)

Various types of Runge-Kutta methods can be devised by employing different numbers of terms in the increment function as specified by n. The first-order RK method with n=1 is, in fact, Euler's method. Once n is chosen, values for the a's, p's, q's are evaluated by setting Equation F6 equal to terms in a Taylor series expansion. Thus, at least for the lower-order versions, the number of terms, n, usually represents the order of the approach. (Chapra and Canale, 2003)

The most popular RK methods are fourth order. There are actually an infinite number of versions for the fourth-order RK method. The following is the most commonly used form, and therefore it is called the classical fourth-order RK method: (Chapra and Canale, 2003)

$$y_{i+1} = y_i + \frac{1}{6}\left(k_1 + 2k_2 + 2k_3 + k_4\right)h \tag{F9}$$

where

$$\begin{aligned}
k_1 &= f\left(x_i, y_i\right) \\
k_2 &= f\left(x_i + \frac{1}{2}h, y_i + \frac{1}{2}k_1 h\right) \\
k_3 &= f\left(x_i + \frac{1}{2}h, y_i + \frac{1}{2}k_2 h\right) \\
k_4 &= f\left(x_i + h, y_i + k_3 h\right)
\end{aligned} \tag{F10}$$

F.2 MATLAB PROGRAMMING

```
% Emulsion Liquid Membrane Extraction Model
% This model was developed based on Lee et al. Model with few
% assumption and simplication

% This model are valid for all system with acidic extractant as a
  carrier
% and acidic solution as a stripping agent
% To run this program, some assumption should be done as stated in
% Chapter 6

% Program Begin

clear

disp('The following equation occurs at interfaces.')
disp('External/membrane interface: A + bB = cC + eH ')
disp('membrane/internal interface: cC + eDH = bB + AD ')
%b = input('b = ');
%c = input('c = ');
%e = input('e = ');
b=1;
c=1;
e=1;

%SR = input('If the stripping reaction is reversible, type 1.\nIf the
stripping reaction is irreversible, type 2.\n');

SR = 2;

if SR == 1

    SR1
elseif SR == 2
    SR2
```

```
else
    disp('Please choose between 1 and 2')
end

% external = input('If mass transfer resistances of ions in the
  external aqueous phase are negligible, type 1.\nElse type 2')

external = 1;

if external == 1;

    %koB = input('koB = ');
    %koC = input('koC = ');
    koB=0.188;
    koC=0.188;

elseif external == 2;
    %koB = input('koB = ');
    %koC = input('koC = ');
    koB=0.188;
    koC=0.188;

    kwA = input('kwA = ');
    kwH = input('kwH = ');
else
    disp('Please choose between 1 and 2')
end



%z = input('If fi1 and fi2 are known, type 1.\nIf VI, VII and VIII are
known, type 2.\n');

z=2;

if z == 1
    fi1 = input('fi1 = ');
%fi1 = volume fraction of internal phase in emulsion drop
    fi2 = input('fi2 = ');
```

```
%fi2 = volume ratio of emulsion phase to the total volume
elseif z == 2
    %VI = input('VI = ');
    %VII = input('VII = ');
    %VIII = input('VIII = ');
    VI=5E-5;
    VII=5E-5;
    VIII=.6E-3;

    fi1 = VI/(VI+VII);
 %fi1 = volume fraction of internal phase in emulsion drop
    fi2 = (VI+VII)/(VI+VII+VIII);
%fi2 = volume ratio of emulsion phase to the total volume
else
    disp('Please choose between 1 and 2')
end

%Rmu = input('Rmu = ');
%R = input('R = ');
R = 7.135E-5;
Rmu = 2.74E-6;

Ri = R - (4*pi/3)^(1/3)*Rmu*(fi1^(-1/3)-1);
delta = R - Ri;
beta = 1 - Ri/R;
fi1_prime = fi1/(1-beta)^3;

%n = input('number of grid points for method of lines = ');

%H_III0 = input('H_III0 = ');
%A_III0 = input('A_III0 = ');
%B0 = input('B0 = ');
%C0 = input('C0 = ');
%H_I0 = input('H_I0 = ');
%A_I0 = input('A_I0 = ');
n=6;
H_I0 = 45;
A_I0 = 0;
```

```
H_III0 = 2.5E-3;
A_III0 = 4.6;
B0 = 5;
C0 = 0;

%Keq = input('Keq = ');

Keq=0.0995;

delta_r = R/(n-1);

H_III = H_III0;
A_III = A_III0;
B = ones(1,n)*B0;
C = ones(1,n)*C0;
A_I = ones(1,n)*A_I0;
H_I = ones(1,n)*H_I0;

H_III_R = H_III0;
A_III_R = A_III0;
B_R = B0;
C_R = C0;

%DeB = input('DeB = ');
%DeC = input('DeC = ');
DeB = 9.187E-8;
DeC = 9.187E-8;

%ML = input('ML = ');
ML_prime=2.093E-9;
ML = ML_prime/(VI+VII+VIII);

t=0;
% time_stop = input('Stop when t = ');
time_stop = 10;
% step_size = input('Step size = ');
step_size = 1E-3;
graph_step_size = 1;
```

```
if external == 1 & b == 1 & c == 1 & e == 1

  for j=0:graph_step_size:time_stop

    while t < j

    h = step_size;   %step size
    RK_NBO

    end

    result = [t A_III/A_III0]

    tt(j+1)=t;
    xx(j+1)=A_III/A_III0;

  end

else

    end


plot(tt,xx)
xlabel('time(s)')
ylabel('Ce/Ceo')
```

```
% slope (method of lines, RUNGE KUTTA)

for RK = 1:4

    if RK == 1

        A_IIIk = A_III;
        H_IIIk = H_III;
        Bk = B;
        Ck = C;
        A_Ik = A_I;
        H_Ik = H_I;

        ext_rxn_1_hkh
        stripping_rxn_1_hkh

    elseif RK == 2 & 3

        Bk(n+1) = [];
        Ck(n+1) = [];

        A_IIIk = A_III + 1/2*dA_III(RK-1,:)*h;
% concentration of A in the external phase at t
        H_IIIk = H_III + 1/2*dH_III(RK-1,:)*h;
% concentration of H in the external phase at t
        Bk = B + 1/2*dB(RK-1,:)*h;
% concentration of B in the emulsion phase for 0 <= r <= Ri at t
        Ck = C + 1/2*dC(RK-1,:)*h;
% concentration of C in the emulsion phase for 0 <= r <= Ri at t
        A_Ik = A_I + 1/2*dA_I(RK-1,:)*h;
% concentration of A in the internal phase for 0 <= r <= Ri at t
        H_Ik = e*A_I0*ones(1,n)+H_I0*ones(1,n)-e*A_Ik;

        ext_rxn_1_hkh
        stripping_rxn_1_hkh

    else
```

```
        Bk(n+1) = [];
        Ck(n+1) = [];

        A_IIIk = A_III + dA_III(RK-1,:)*h;
% concentration of A in the external phase at t
        H_IIIk = H_III + dH_III(RK-1,:)*h;
% concentration of H in the external phase at t
        Bk = B + dB(RK-1,:)*h;
% concentration of B in the emulsion phase for 0 <= r <= Ri at t
        Ck = C + dC(RK-1,:)*h;
% concentration of C in the emulsion phase for 0 <= r <= Ri at t
        A_Ik = A_I + dA_I(RK-1,:)*h;
% concentration of A in the internal phase for 0 <= r <= Ri at t
        H_Ik = e*A_I0*ones(1,n)+H_I0*ones(1,n)-e*A_Ik;

        ext_rxn_1_hkh
        stripping_rxn_1_hkh

    end



    dA_IIIk = -1/(1-fi2)*(3*fi2/R*koC*(C_R-Ck(n))/c-ML*A_Ik(n));
    dH_IIIk = 1/(1-fi2)*(3*fi2/R*koC*(C_R-Ck(n))*e/c+ML*H_Ik(n));

    dA_III(RK,1) = dA_IIIk;
    dH_III(RK,1) = dH_IIIk;

    Ck(n+1) = 2*delta_r*koC*(C_R-Ck(n))/DeC + Ck(n-1);
% imaginary point
    Bk(n+1) = 2*delta_r*koB*(B_R-Bk(n))/DeB + Bk(n-1);
% imaginary point

    for p = 1:n
        if p == 1
            dBpk = 1/(1-fi1_prime)*(DeB*6*(Bk(p+1)-
                   Bk(p))/delta_r^2+3*fi1_prime/Rmu*b*rri(p));
            dCpk = 1/(1-fi1_prime)*(DeC*6*(Ck(p+1)-Ck(p))/delta_r^2-
                   3*fi1_prime/Rmu*c*rri(p));
```

```
        else
            dBpk = 1/(1-fi1_prime)*(DeB*(1/delta_r^2*(Bk(p+1)-
                   2*Bk(p)+Bk(p-1))+1/(p-1)/delta_r^2*(Bk(p+1)-Bk(p-
                   1)))+3*fi1_prime/Rmu*b*rri(p));
            dCpk = 1/(1-fi1_prime)*(DeC*(1/delta_r^2*(Ck(p+1)-
                   2*Ck(p)+Ck(p-1))+1/(p-1)/delta_r^2*(Ck(p+1)-Ck(p-
                   1)))-3*fi1_prime/Rmu*c*rri(p));
        end

        dB(RK,p) = dBpk;
        dC(RK,p) = dCpk;
    end

    dA_Ik = 3/Rmu*rri;
    dA_I(RK,:) = dA_Ik;

end

t = t+h;

A_III = A_III +
1/6*(dA_III(1,:)+2*dA_III(2,:)+2*dA_III(3,:)+dA_III(4,:))*h;
% concentration of A in the external phase at t
H_III = H_III +
1/6*(dH_III(1,:)+2*dH_III(2,:)+2*dH_III(3,:)+dH_III(4,:))*h;
% concentration of H in the external phase at t
B = B + 1/6*(dB(1,:)+2*dB(2,:)+2*dB(3,:)+dB(4,:))*h;
% concentration of B in the emulsion phase for 0 <= r <= Ri at t
C = C + 1/6*(dC(1,:)+2*dC(2,:)+2*dC(3,:)+dC(4,:))*h;
% concentration of C in the emulsion phase for 0 <= r <= Ri at t
A_I = A_I + 1/6*(dA_I(1,:)+2*dA_I(2,:)+2*dA_I(3,:)+dA_I(4,:))*h;
% concentration of A in the internal phase for 0 <= r <= Ri at t
H_I = e*A_I0*ones(1,n)+H_I0*ones(1,n)-e*A_I;
```

```
disp('The reverse reaction rate or stripping reaction rate is:')
disp('rr = kr.*(A_I.^a1).*(B.^b1).*(C.^c1).*(H_I.^e1)')
disp('Please insert value of a1, b1, c1, e1 and kr')

%a1 = input('a1 = ');
%b1 = input('b1 = ');
%c1 = input('c1 = ');
%e1 = input('e1 = ');
%kr = input('kr = ');
a1=0;
b1=0;
c1=1;
e1=1;
kr=1.225E-8;

rr = inline('kr.*(A_I.^a1).*(B.^b1).*(C.^c1).*(H_I.^e1)');



% stripping reaction for irreversible process
rri = rr(A_Ik,Bk,Ck,H_Ik,a1,b1,c1,e1,kr);



%interfacial values for b=1,c=1,e=1 and no aqueous mass transfer
resistance
C_R = Keq*A_IIIk*B0/(H_IIIk + Keq*A_IIIk); % concentration of complex
at r=R
B_R = B0 - C_R;                         % concentration of carrier at
r=R
```