CHAPTER 3

METHODOLOGY

3.1. Chemicals

3.1.1. Chemicals used in ELM preparation

Generally, ELM comprises four components, as described in Chapter 2. However, in the present study, $[BMIM]^+[NTf_2]^-$ has been incorporated in the system as a stabilizer. Therefore, five components were present in the ELM system.

3.1.1.1. Solvent

Kerosene from ACROS (USA) of boiling point range 180 - 280 °C was used as solvent for the ELM system. It was selected because it is readily available and its lower cost. Another reason for this selection was that it is less toxic in comparison to other solvents such as toluene and chloroform. It was used in its raw form, i.e. without further purification.

3.1.1.2. Surfactant

Surfactant plays an important role since its type and concentration affect the stability, and hence the removal efficiency of ELM. SPAN 80, a non ionic surfactant, was selected to provide stability to the ELM system. HLB, the hydrophilic to lipophilic balance value of SPAN 80 is 4.3 which makes it more soluble in the organic phase (kerosene) rather than in the internal phase. This property of SPAN 80 eliminates the possibility of using other types of surfactant. SPAN 80 was purchased directly from Merck (Malaysia).

3.1.1.3. Carrier

As mentioned earlier, Type-II facilitation involves a carrier which forms a complex with a metal ion. The complex travels through the membrane phase to reach the inner interface. The internal reagent reacts with the complex and yields a salt and the carrier. The unaltered carrier diffuses back to the membrane phase for further extraction to take place. The rate of extraction is highly dependent on the type and the concentration of the carrier. Therefore, a comprehensive theoretical research was carried out to find an optimum carrier for the process.

There are a number of carriers for the removal of metal ions using Type-II facilitation in the ELM process. Their properties such as viscosity, density and solubility in aqueous phase impact the overall removal efficiency of the ELM process. Since the carrier reacts with the metal ions to form a complex at the outer interface, the electron donor group of the carrier plays a vital role to form the complex. It was found that most of the carriers have P=O donor group which has a substantial amount of polarity to carry out the donation of electrons to electron deficient metal ions. Table 3.1 lists such carrier, e.g. TOPO (Cyanex921), Cyanex 923, Bis –(2-ethylhexyl)-phosphate (D2EHPA) or DEHPA and Tri n-butyl phosphate. The other types of carriers are quaternary ammonium salts such as Aliquat 336 and TOMAC which contain e^- deficient nitrogen group. The reaction between the metal and the carrier is called cation-anion displacement reaction. The third type of carriers is amine group which has a lone pair of electrons on the nitrogen atom which easily forms a ligand with the electron deficient metal. All the properties of the carriers are mentioned in Table 3.1.

Table 3.1: Some important properties of all of the above mentioned extractants.

Extractant	Density/specific gravity at 25°C (gm/cm^3)	Viscosity (cP)	Polar bond	Boiling point °C	Solubility in water (mg/L)
TOPO or Hygroscopic Cyanex921	0.88	N/A	P=O bond	201-202	
Cyanex 923	0.88	40 at 25°C 13.7 at 50°C	P=O bond	310	>10
D2EHPA	0.96	28.59 at 27	P=O bond	209	1000
Aliquat 336 30°C	0.88	1500 at 25°C	Quaternary ammonium salt	225	0.12 at 0.2 at 60°C
Tertiary amine N7301	0.81	10.5 at 25°C	R_3N R = C_nH_{2n+1}, n = 8–10	N/A	<.01 9
Tri octyl amine	0.80-0.81	15 at 25°C	$(C_8H_{17})_3N$	365-367	N/A
Alamine 336	0.81	23 at 40°C 11 at 86°C 6 at 140°C	Tri octyl/ decyl amine	N/A	<5
Tri n-butyl Insoluble phosphate	0.97	3.5-12.2	P=O bond	289	
Tri-n-dodecyl-amine	0.82	N/A	N/A	220-228	N/A
Tri-n-hexyl-Amine	0.79	N/A	N/A	150-159	N/A
Di-nonyl-naphthalene sulfonic acid	N/A	N/A	N/A	600.4°	N/A

N/A : Not Available

Cation-anion reactions are generally very fast in comparison to ligand formation. This is attributed to the presence of strong electrostatic interactions. Therefore, the complex formation by TOMAC is relatively faster than by other carriers, either having a P=O group or an amine group.

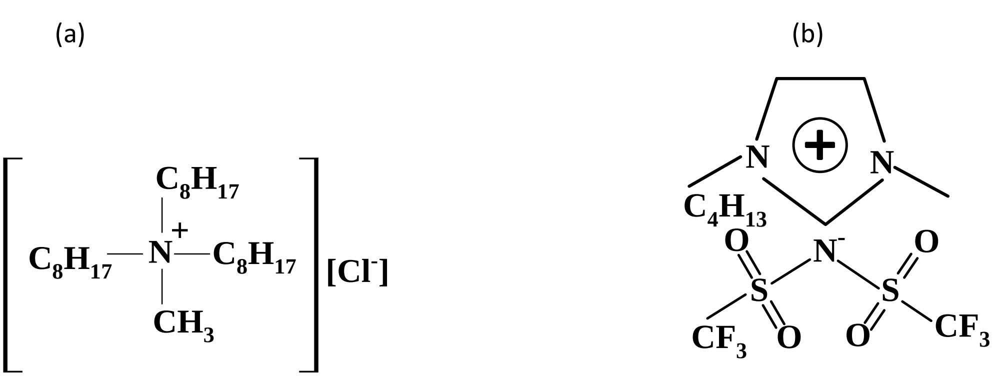
The economy of the ELM process is highly dependent on the amount of carrier used. TOMAC, with structural formula illustrated in Fig.3.1 (a), is inexpensive and is relatively less toxic. Therefore, TOMAC, obtained from Merck (Germany), was selected as a carrier for the ELM process.

3.1.1.4. Internal reagent

NaOH was chosen as an internal reagent to strip the metal ion from the complex. The reason for this selection is to create a pH difference between the feed phase and the internal phase. Sodium hydroxide pellets were supplied by R&M Chemicals (UK).

3.1.1.5. Stabilizer ($[BMIM]^+[NTf_2]^-$)

Ionic liquid $[BMIM]^+[NTf_2]^-$, with structural formula illustrated in Fig.3.1 (b), was chosen over other ionic liquids due to its hydrophobicity, minimum toxicity, relatively lower viscosity and density. $[BMIM]^+[NTf_2]^-$ was procured from Merck (Germany).



TOMAC $[BMIM]^+[NTf_2]^-$

Figure 3.1 Structures of TOMAC and $[BMIM]^+[NTf_2]^-$.

3.1.2. Chemicals used in feed phase

3.1.2.1. Feed solution

Feed solution is an aqueous phase containing potassium dichromate and HCl acid. HCl is added in the feed phase to keep an optimal initial pH. Potassium dichromate and hydrochloric acid were received from R&M Chemicals (UK). Doubly distilled de-ionized water was used to prepare the feed phase.

3.2. Emulsion liquid membrane preparation and extraction

3.2.1. Preparation of Emulsion Liquid Membrane

The ELM microscopically contains two phases and five components. However, it appears as a homogeneous phase macroscopically. The solvent and the internal reagent are two phases. The carrier and the stabilizer ($[BMIM]^+[NTf_2]^-$) remain in the solvent phase while the surfactant either remain at the interface between the solvent and the feed phase or in the solvent phase as reverse micelles.

The emulsion was prepared in a 100 mL unbaffled beaker by mixing organic solvent and an appropriate amount of non ionic surfactant Span 80. Subsequently, the carrier and the ionic liquid (stabilizer) were added to the mixture. The mixture was then homogenized for up to 5 minutes by using a motor driven homogenizer (IKA, model: T25 digtal Ultra Turrax) at a speed ranging from 4000 to 10000 rpm. NaOH of a known molarity was added drop-wise into the mixture while keeping the whole mixture homogenized for the next 5 minutes. A homogeneous milky white emulsion was obtained. The emulsion was either taken for stability analysis or for the extraction of Cr.

3.2.2. Extraction of Cr

The feed phase was prepared by dissolving an appropriate amount of potassium dichromate in doubly distilled de-ionized water, and its pH was varied using HCl. In order to investigate the effect of the various parameters on the % removal efficiency of the ELM process, the prepared emulsion was poured into another 250 mL beaker containing the Cr solution. The concentration of Cr solution was kept at a fixed value of 100 mg/L (100 ppm) unless otherwise stated. The pH of the feed phase was maintained below 1.5 so as to establish a pH difference between the internal and external phases, and this provided a driving force for Cr to diffuse through the membrane during the process.

The mixture was gently stirred by using a mechanical stirrer and an agitation speed of 300 rpm was found to be optimal for the generation of fine globules of emulsion with the lowest possible breakage (discussed in Chapter 4). Samples were taken at a regular interval using disposable syringes and the syringes were left undisturbed for a period of time until the emulsion and the feed phase were separated. Thereafter, the feed phase samples were analyzed for the remaining % of Cr. The % removal efficiency of the ELM process was calculated using the following expression:

$$\%\ \text{Removal efficiency} = \frac{C_i - C_f}{C_i}\ X\ 100$$

where, c_i and c_f are initial and final concentration of the feed phase, respectively.

3.3. Emulsion liquid membrane stability analysis

The stability analysis of ELM was carried out in order to identify the role of ionic liquid $[BMIM]^+[NTf_2]^-$. The prepared emulsion was kept for 3 h and photographs of the emulsion were taken at regular intervals, and these were analyzed by using AUTOCAD. The interface height variation of the emulsion with respect to time was studied, and the rate of phase separation of the emulsion was calculated. Care was taken to ensure that there was no perturbation in the beaker during photography, and that there was no change in the level of the camera's height and the beaker from the ground level.

3.4. Analytical Procedures

3.4.1. Chromium analysis

Chromium concentration in the feed phase was measured by using an inductively coupled plasma spectrophotometer (ICP, PerkinElmer, model: Optima 7000DV). The samples were diluted to make them up to the required volume needed by ICP. Standard solutions of 10, 50, 80 and 100 mg/L were prepared. The QC analysis was done at the value of 80 mg/L. The final concentration of the feed phase given by ICP was multiplied by the dilution factor to obtain the original final concentration.

3.4.2. pH measurement

The pH of the feed phase and the samples were calculated by using a CyberScan 510 pH meter. All the pH measurements were carried out at room temperature.

3.4.3. Surface tension measurement

Surface tension measurement was chosen to determine the CMC (Critical Micelle Concentration) of the surfactant. The surface tension of kerosene containing ionic liquid was calculated in order to identify the role of ionic liquid $[BMIM]^+[NTf_2]^-$. The effect of

TOMAC on the surface tension of ionic liquid $[BMIM]^+[NTf_2]^-$ was calculated in order to determine the behaviour of TOMAC on the surface of $[BMIM]^+[NTf_2]^-$. Surface tension was measured by a tensiometer (Fisher Scientific, model: Tensiomat 21®) using a Pt/Ir Du Noüy ring at room temperature.

3.4.4. Measurement of globule size and internal droplet in ELM

Emulsion drop size measurement was accomplished by using a microscope with an attached camera. A very fine drop of emulsion was placed on a glass slide and was covered by a glass slip in order to get a clear image of the internal droplets and the globules. The images were analyzed and an average value for both of the quantities was calculated.

3.4.5. Error analysis

Error analysis is a very important aspect of any research work in order to verify its validity. Sometimes, it is used to determine the effectiveness of a mathematical model for a process with respect to the experimental work. In the present study, since parameters were optimized by using experimental work and response surface methodology, it became necessary to do the error analysis to evaluate the performance of the model obtained by response surface method. The error for each parameter was calculated by the following equation:

$$\text{Error} = \frac{Predicted\ value - Experimental\ value}{Experimental\ value}$$

An absolute value was taken in order to make a comparison of errors.