

## **CHAPTER 2**

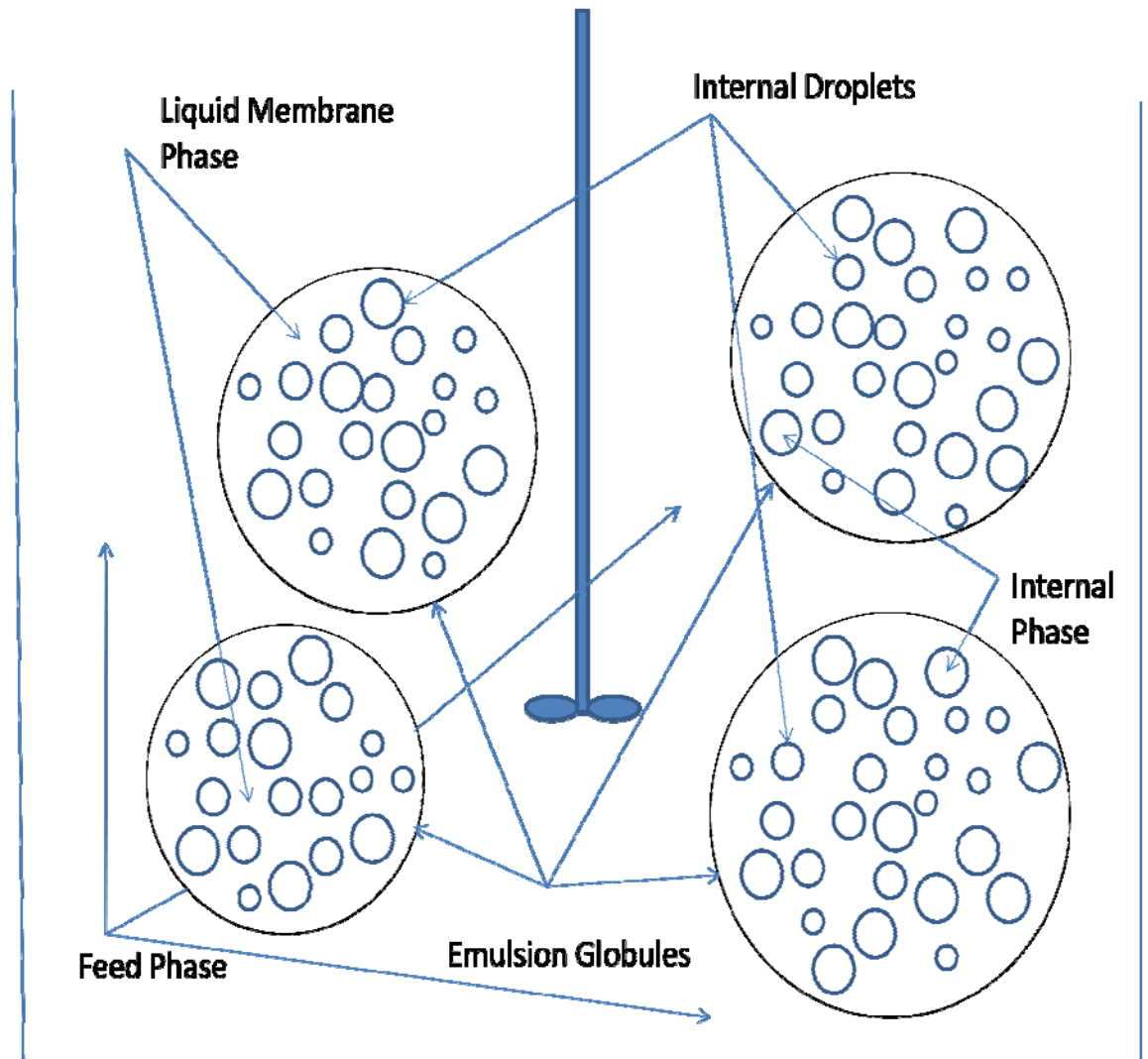
### **LITERATURE REVIEW**

#### **2.1. Emulsion Liquid Membranes (ELMs)**

Emulsion liquid membrane (ELM) is a form of common emulsions that we encounter in daily life such as food emulsions, cosmetic emulsions, pharmaceutical emulsions and perfluorochemical emulsions. ELM has received a wide recognition due to their extraordinary capability to recover heavy metals (Mortaheb et al., 2009), organic compounds (Chakrabarty et al., 2010) and numerous pharmaceutical compounds (Sahoo and Dutta, 1998). Since the discovery of ELM by Norman Li (Li, 1968), it is always preferred over solvent extraction due to its low cost operation, minimum energy consumption and single stage operation. Extraction and stripping reactions take place simultaneously in ELM.

ELM is made of an aqueous phase generally referred to as a receptor or an internal phase which is surrounded by an oil phase (membrane phase). The internal phase resides in the oil phase as fine droplets of diameter 1-10  $\mu\text{m}$  (Park Y., et al., 2006). Generally, the internal droplets are poly-dispersed in the oil phase but due to their very small diameters the whole system looks like a homogeneous system (W/O). These internal droplets are stabilized by a surfactant or co-surfactant or stabilizer (Williams, 1991). This homogeneous system is further dispersed in another phase referred to as feed phase (donor phase) to make a three phase system (W/O/W). (W/O) phase is spread as fine globules of diameter 0.1-2 mm in the feed phase (Gallego-Lizon and Pacrez de Ortiz, 2000). Feed phase contains the solute or target metal or compound to be extracted and stripped. A gentle stirring is provided to the W/O/W system to make the distribution of globules

uniform throughout the mixture. Solute is transferred from the feed phase to the internal phase through the membrane phase. Oil phase or membrane phase acts as a wall in the mass transfer of solute from the feed phase to the internal phase and selectively allowing solute to pass through it (Lin and Long, 1997). Thus, ELMs are very selective depending on their compositions. A schematic of the ELM process is as shown in Fig. 2.1.



**Figure 2.1** Emulsion globules and internal droplets in a (W/O/W) ELM system.

The driving forces for solute transfer are the concentration difference of the solute between the internal phase and the feed phase, the pH difference between the internal and

the feed phase and osmotic pressure difference between the internal and the feed phase (Devulapalli and Jones, 1999; Itoh et al., 1990; Kargari et al., 2004). Trapped solutes in the internal phase are converted into either a salt or some other compound to maintain a healthy difference of concentration between the feed phase and the internal phase throughout the operation. However, as the concentration of solute in the feed phase decreases, the concentration gradient decreases automatically. Eventually, the concentration gradient becomes zero and the mass transfer stops.

## **2.2. Types of ELM**

ELMs have been assorted mainly into two categories depending on the presence of a carrier in its oil phase. However, the driving force to transfer the solute from the feed phase to the internal phase remains as the concentration gradient (chemical potential) between the feed phase and the membrane phase (Skelland and Meng, 1999). The selection of the type of ELM depends on the solubility of the solute in the oil phase and on the rate of extraction.

### **2.2.1. Type - I ELM**

Type-I ELM system does not contain any carrier in the membrane phase. The important condition for an ELM to be a Type-I ELM is that the solute must be soluble to all three phases: donor phase, membrane phase and receptor phase (Correia and Carvalho, 2000). In this type of ELM system, the solute first comes to the interface of the feed phase and the membrane phase (outer interface). Due to its solubility in the membrane phase, the membrane allows it to pass through the interface. Subsequently, it diffuses through the membrane due to the difference of chemical potential between the membrane and the

internal phase. It reaches at the interface of the membrane phase and the internal phase (inner interface). It is stripped at the inner interface by an internal reagent. This reaction is called the stripping reaction. The reaction between the solute and the internal reagent yields a compound which is not soluble in the membrane phase and cannot diffuse back in the membrane phase. Consequently, the solute is trapped in the internal phase (Yan et al.,1992).

Devulapalli and Jones (1999) reported the removal of aniline from the feed phase using HCl as internal reagent without using any carrier. The membrane phase was prepared by using kerosene as solvent and span 80 as surfactant. It is a good example of Type-I ELM as aniline is soluble in kerosene. The difference in pH between the feed phase and the internal phase plays the role of the driving force for the diffusion of aniline through the membrane phase. Once the solute reaches at the inner interface, it is stripped through the reaction with HCl. It converts into  $C_6H_5NH_3^+Cl^-$  which is insoluble in the membrane phase and the aniline is entrapped in the internal phase. The rate of removal can be enhanced by varying the pH of either the feed phase or the internal phase.

### **2.2.2. Type - II ELM**

Type-II ELM system contains a carrier in the membrane phase of ELM. This system is advantageous when the solute present in the feed phase is not soluble in the membrane phase (Li, 1978). In Type-II ELM system, the carrier reacts with the solute and forms a complex at the outer interface. The complex, being soluble in the membrane phase, diffuses through the oil phase and reaches the inner interface where the reaction between the complex and the internal reagent occurs. The reaction converts the complex into two compounds; one being the carrier itself and the other is a salt or ion which is insoluble in

the membrane phase. The carrier diffuses back into the membrane phase and again participates in the reaction for complex formation, thus forwarding the removal rate of the solute. The salt or ion remains in the internal phase as stripped solutes. Type-II ELMs are referred as “Carrier mediated” transport because the solute is transferred by the help of a carrier (Ho et al., 1982).

It can be deduced from the above discussion that the rate of removal in Type-II ELM depends on the rate of formation of the complex at the outer interface and the rate of stripping of the complex at the inner interface. Lin and Long (1997) suggested that the driving force in Type-II facilitation is the concentration gradient of the solute-carrier complex at the outer interface and the inner interface. Therefore, a higher rate of stripping is always preferred to maintain a concentration gradient of the complex between the outer and the inner interface. Apart from the complex concentration gradient, pH difference between the feed phase and the internal phase was also found to affect the % removal of solute (Kargari et al., 2004).

In this study, Cr has been removed from wastewater by employing Type-II facilitation. The feed phase was kept highly acidic and on the opposite side, the receptor phase was maintained as a basic medium. The pH difference between the phases drives the metal ions to form complexes at the outer interface, and are stripped at the inner interface. However, the pH difference depletes with time and eventually vanishes when either all the internal reagent finishes or all the metal ions are transferred to the stripping phase.

### **2.3. Emulsion Liquid Membrane: The whole process**

In order to understand the complete ELM process, first of all, we need to go through each and every constitutional step. All of these steps are equally important to make the process

efficient and economical. ELM process contains three major steps, as shown in Fig 2.2.

These steps are:

- (i). ELM preparation
- (ii). Extraction and stripping of the solute from the feed phase
- (iii). Demulsification

### **2.3.1. ELM preparation**

ELM preparation is the first and the most important step of the whole ELM process. In this process, all the components of the ELM are mixed under a high speed homogenizer. The types and the concentrations of the components are dependent upon the application of ELM, type of solute and the feed phase.

Generally, ELM contains four major components: solvent, surfactant or co-surfactant, internal reagent and carrier (for Type-II facilitation). However, ELM preparation does not restrict itself to only these four components. Depending upon the process, there is always a possibility of the inclusion of other stabilizers, polymers and metals. The inclusion of these components completely depends on their functionalities and on the requirement of the system.

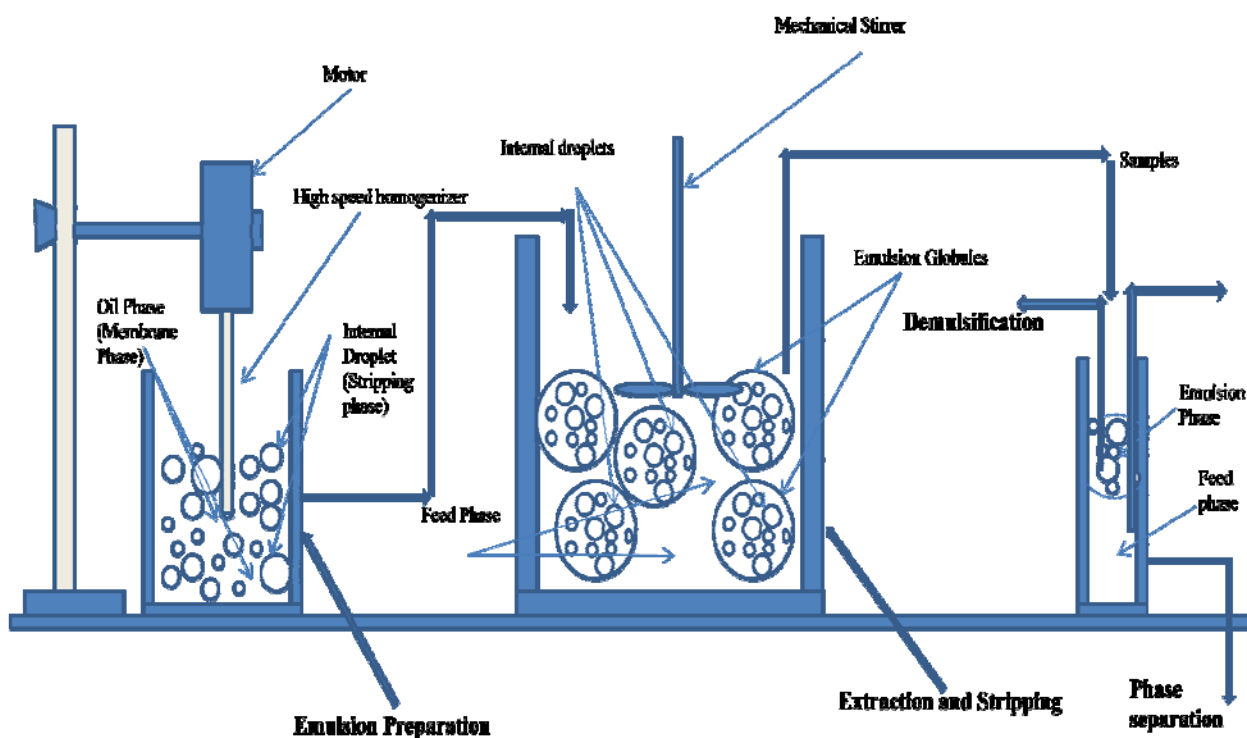
The preparation of ELM comprises two steps: (i) membrane preparation, and (ii) drop-wise addition of the internal reagent. The description of these steps is as follows:

(i) **Membrane preparation:** Appropriate amounts of solvent, surfactant and carrier are taken in a beaker and homogenized at a high speed until they are well mixed. The most important part in this step is to select a suitable solvent. The type of ELM process determines the selection of the solvent. The properties to be considered before choosing a solvent are well described by Ho and Sirkar (Ho and Sirkar, 1992). These properties are

low solubility of the solvent in the feed and the internal phase, limited viscosity such that the diffusion of solute-carrier complex is not affected, compatible with surfactant and carrier and low cost production. In the present study, kerosene with a boiling point range of 180-280 °C was selected due to its compliance with the above mentioned properties.

Another important selection that plays a key role in the stability of ELM is the selection of a suitable surfactant for the ELM process (Binks et al., 1999). The role of the surfactant is not only to provide stability to the ELM but also to minimize the breakage of the internal droplets (Kargari et al., 2004). However, a large amount of surfactant concentration causes swelling of the ELM which increases the volume of the internal droplets. As a result, the internal droplets break and the stripped solutes diffuse back to the feed phase (Yan and Pal, 2001). Thus, an appropriate surfactant and its concentration is vital to achieve the maximum removal efficiency in the ELM process. In addition, according to Draxler and Marr (1986), surfactant also affects several other parameters such as osmosis, water solubility and mass transfer

The required properties of a surfactant which are necessary to prepare a stable and efficient ELM (Mok et al., 1996; Shen et al., 1996) are: it should be inactive with a carrier to avoid any modification in their properties, it should be more soluble in the membrane phase, its CMC (Critical Micelle concentration) should be high enough to avoid any early CMC formation as they promote swelling of the ELM and it should create less mass transfer resistance for the transport of the complex.



**Figure 2.2** Schematic of emulsion liquid membrane process.

Carrier selectivity of the ELM process depends on the thermodynamics and kinetic properties of the extraction reaction at the outer interface and also on the stripping reaction at the inner interface (Kulkarni and Mahajani, 2002). It should react thermodynamically with the solute to form a complex and the complex should react kinetically with the internal reagent to release the metal in the internal phase (Bhowal and Datta, 2001). The more stable complex in the membrane phase is preferred to extract the solute with a fast rate. TOMAC was selected as a carrier for the present study to remove chromium from the feed phase. The reasons for choosing TOMAC are its reversible reaction with Cr metal ion at the outer interface of the ELM (Venkatesan and Meera Sheriffa Begum, 2009), and this reaction is thermodynamically stable. Another reason of choosing TOMAC is that TOMAC-Cr complex reacts instantly with the internal reagent that maintains a sharp



chemical potential difference between the outer and the inner interface. Hence, the driving force is maintained to transport the complex through the membrane phase.

(ii) **Drop-wise addition of the internal reagent:** After mixing the solvent, the carrier and the surfactant adequately, internal reagent is added to the mixture. The addition of internal droplets can be done either drop-wise or by just pouring NaOH into the mixture. The mixture is again homogenized at a very high speed in the range of 4000-10000 rpm until a milky white solution is obtained. The internal reagent is crucial in the selection for the ELM. Kumbasar and Sahin (2008) suggested some properties of internal reagents, and these are they should not be soluble in solvent, they should be inactive or least inactive with the surfactant, they should react fast and kinetically with the complex and they should be less expensive.

### **2.3.2. Extraction and stripping of the solute from the feed phase**

In this step, the prepared emulsion is dispersed into the third phase or feed phase by using a mechanical stirrer. The stirring speed is varied in the range of 100 - 400 rpm until emulsion globules of diameter of size 0.1-2 mm are generated (Skelland and Lee, 1981). At high agitation speed, the size of the globules decreases and hence the interfacial area between the feed phase and the membrane phase increases, thus the rate of extraction increases. Nonetheless, further increase in the agitation speed enhances the shear rate and shear stress which causes membrane breakage and reduces the stability.

### **2.3.3. Demulsification**

Demulsification is the process that defines the overall effective cost of the operation. If all the key components of ELM are recovered along with the solute then the process is highly

economical. There are two methods of demulsifying the ELM, namely chemical treatment and physical treatment (Ho and Sirkar, 1992). Chemical treatment involves an addition of demulsifier in the ELM. This is the easiest way to separate the phases but it changes the properties of the solvent, surfactant and carrier. After the chemical treatment the components cannot be reused. Physical treatment includes heating, centrifugation, ultrasonication, solvent dissolution, high shear, microwave radiation, and the use of high-voltage electrostatic fields.

#### **2.4. Stability and swelling of ELM**

Swelling and instability are two major concerns that hinder the effective use of ELM to separate the organic compounds and heavy metals (Nakashio et al., 1988). Swelling occurs when water molecules present in the external aqueous phase (W/O/W) permeates through the membrane phase and reaches into the internal phase. This process not only increases the volume of the internal phase but also dilutes the concentration of the separated solute which reduces the overall efficiency of the extraction. Sometimes, due to the excessive transport of water molecules in the internal phase, the breakage of emulsion globule occurs and this nullifies the overall extraction. In the literature (Kinugasa et al., 1989), two types of swellings have been reported: osmotic swelling and entrainment swelling. Water transport by osmotic swelling comprises molecular diffusion of water molecules, micelles assisted transport of water molecules, and hydration at the outer interface followed by dehydration at the inner interface of surfactant molecule (Colinart et al., 1984; Garti, et al., 1985). On the other hand, entrainment swelling combines entrainment and secondary emulsification of the water molecules present in the external phase due to excessive surfactant (Kinugasa et al., 1989; Skelland and Meng, 1999).

The stability of the ELM is generally defined as its enduringness under high shear and high stress during the of extraction process. According to Binks (1998) and Skelland and Meng (1996), if the ELM is not resistant enough to breakage or rupture, then it starts to crumple. The stripped solute inside the internal phase oozes out of the membrane and mixes with the feed phase, hence the overall efficiency of the membrane decreases. The four fundamental ways by which an emulsion may become unstable are creaming or sedimenting, flocculation, coalescence and Ostwald ripening.

The effects of first three processes on the ELM stability are very difficult to avoid completely. However, creaming may be reduced by minimizing the density difference between the internal phase and the membrane phase and by dispersing very fine droplets of the internal phase throughout the membrane phase (Binks, 1998) .

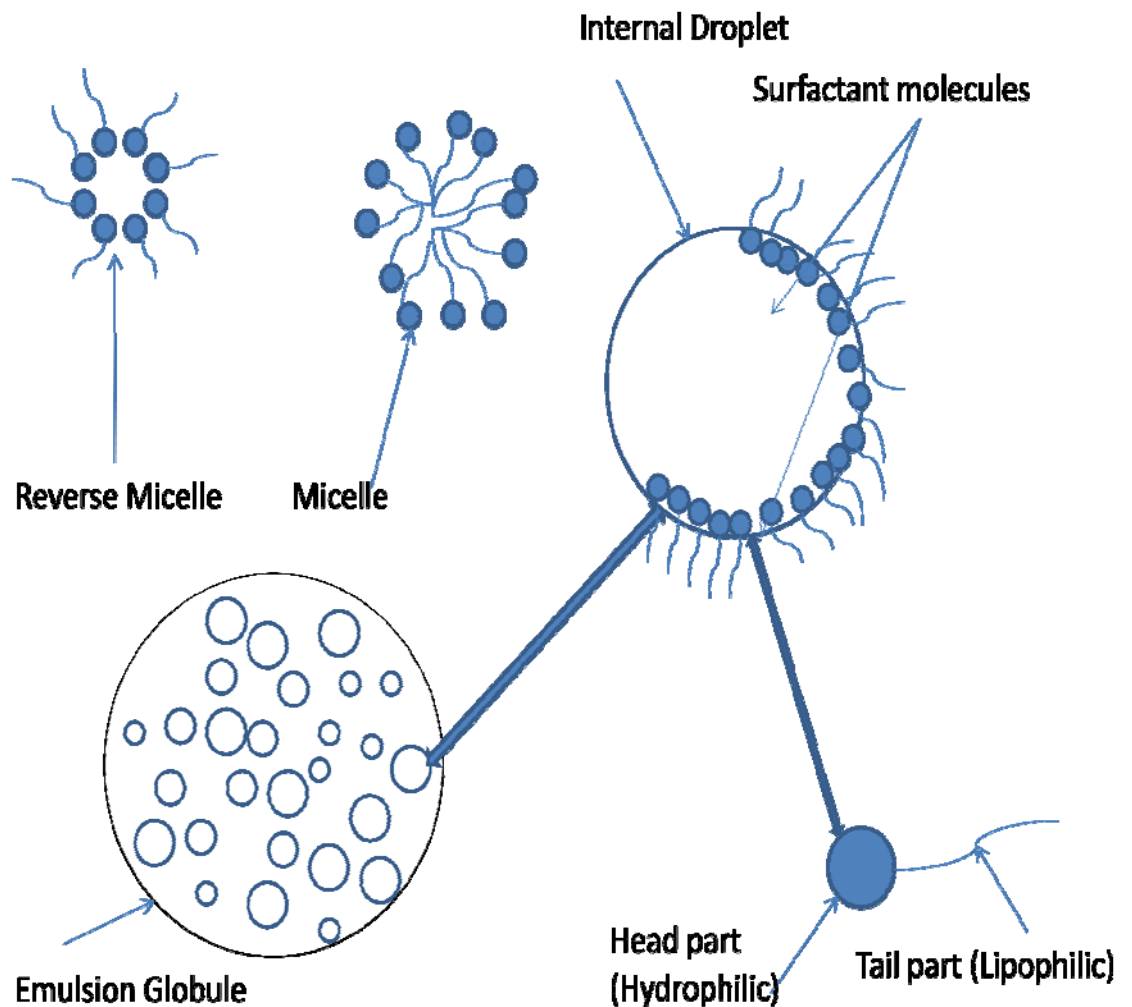
Flocculation is caused by poly-dispersity of globules and surfactant concentration above CMC. Therefore, mono dispersion of the internal droplets and the surfactant concentration below CMC are favorable conditions to minimize flocculation (Zhao and Bai, 2009).

Coalescence occurs when the forces between the internal droplets surfaces are such that the film of continuous phase between them becomes sufficiently thin such that the film ruptures (Calabrese et al., 1986). Coalescence is an irreversible phenomenon. It is highly dependent on the hydrodynamics of the film flow and the forces acting across it (Lepercq-Bost et al., 2010). Physically, it was found that surfactant molecules make a protective layer over internal droplets and it saves them not only from high shear but also from coalescence up to a certain extent.

Ostwald ripening is the growth of bigger internal droplets at the expense of smaller internal droplets. The reason for this phenomenon has been explained by Gibbs–Thomsan’s theorem which states that smaller internal droplets have higher chemical

potential than the bigger ones (De Smet et al., 1999). The difference in the chemical potential between bigger and smaller droplets generates a driving force. The molecules from the smaller droplets travel through the membrane and attach themselves to the bigger ones (Jiao and Burgess, 2003). According to Hoang et al. (2001), Jiao and Burgess (2003) and Taylor (1995), the extent of Ostwald ripening is dependent on the solubility of the internal phase in the membrane phase.

The solubility of the internal phase in the membrane phase is a key factor to induce Ostwald ripening in the system (Neogi and Narsimhan, 2001). If both of the phases are completely insoluble in each other, then the possibility of Ostwald ripening can be deflected (Taylor, 2003). In the present study, aqueous NaOH and kerosene were selected as the internal and the membrane phase respectively. They are almost insoluble in each other, hence Ostwald ripening was the least possible mean for the ELM to destabilize. However, surfactants present in the membrane phase may enhance the solubility of the internal phase in the membrane phase by forming micelles and reverse micelles, as shown in Fig. 2.3. Thus, Ostwald ripening may cause the ELM to become unstable but as mentioned earlier, the surfactant concentration was kept below CMC. As a result, for the present work precautions were taken for all the factors which can induce Ostwald ripening.



**Figure 2.3** Surfactants orientation in an emulsion globule

Several remedies were discovered to overcome the stability and swelling problems, such as the use of aliphatic solvent instead of aromatic solvent (Nakashio et al., 1988), the increment of carbon chain length of aliphatic solvent (Kinugasa et al., 1989), increment of the surfactant concentration (Hsu and Li, 1985), the increment of membrane viscosity (Terry et al., 1982; Kinugasa et al., 1989), by the addition of various stabilizers such as paraffin, cyclohexane, n-decanol, and 1-decanol, the use of co-surfactant which can balance the HLB (hydrophilic/lipophilic) ratio (Mok et al.1996), non-Newtonian conversion of the membrane phase (Skelland and Meng, 1999), the use of Janus particles as stabilizers in emulsion polymerization (Muller et al., 2008), stability provided by

functionalized silica particles for high internal phase emulsion (Bismarck et al., 2008). All of the remedies have their own tradeoffs and compromises with the overall extraction efficiency.

## **2.5. Chromium**

Hexavalent Cr is a very toxic form of the Cr metal as compare to trivalent Cr (III) due to its oxidizing nature. Cr (VI) is not only carcinogenic but causes many serious health problems to the biological system such as nose bleeding, respiratory problems and skin rashes (Arslan et al., 2009; Chiha et al., 2006; Zouhri et al., 1999). Cr (VI) also affects wild life in a significant amount that has raised serious concerns in our eco-system. World Health Organization has declared Cr (VI) removal from wastewater as a serious and prime research topic in 1998 meeting held in Geneva. In biological systems, Cr (III) is in trace amounts whereas Cr (VI) is considered to be toxic even at very low concentrations (US: EPA, 1998). The development of new technologies for the removal of Cr is progressing day by day.

Industries which release a large amount of Cr (VI) through wastewater are electroplating, leather tanning, aluminium conversion coating operations, textile mills, pigment industries and wood preservative industries (Barnhart, 1997). “In view of the contrasting effects of Cr species and of the possible changes of Cr oxidation state, a limit for ‘total dissolved Cr’ in natural water has been set at 50 ppb by the US, the EU, Canada, Russia, Japan, and many other countries”(Giusti and Barakat, 2005).

## 2.6. Ionic Liquids

Room temperature ionic liquids (RTILs) possess unique and exceptional properties such as negligible vapour pressure, inflammability, thermal stability even at high temperatures, highly polar yet non-coordinating solvent and application based adjustable miscibility/immiscibility in chemical processes (Earle, 2000; Freemantle, 2001; Holbrey and Seddon, 1999; Mikami, 2005; Wasserscheid and Welton, 2008; Welton, 1999). These properties have made them potentially useful in a wide range of applications in industries as well as in research. Ionic liquids possess a very negligible vapour pressure that has enabled them to be used as a “green solvent” in synthesis (Seddon et al., 1998; Welton et al., 1999; Song and Roh, 2000; Wasserscheid and Welton, 2008; Welton, 1999), separation and purification (Branco et al., 2002; Dai et al., 1999; de los Rios et al., 2010; Fadeev and Meagher, 2001; Sun and Hussey, 1989; Visser et al., 2000; Visser et al., 2001) and electrochemical application (Sun and Hussey, 1989). RTILs being stable and in the liquid form at room temperature, are made of organic cations and organic or inorganic anions. The physical and chemical properties of RTILs can be altered by changing the cation or anion or both to facilitate a particular task. Hence, they are sometimes referred as “task specific” ionic liquids (Wasserscheid and Welton, 2008) .

Nevertheless, very few studies have been reported on the application of ionic liquids in ELM. Thus, an effort to incorporate ionic liquids with emulsion liquid membrane has been made by investigating the stability and % removal efficiency of emulsion liquid membrane in the presence of ionic liquid [BMIM]<sup>+</sup>[NTf<sub>2</sub>]<sup>-</sup>.

## 2.7. Ionic liquids in emulsions

Ionic liquids fulfill the criterion for environmentally friendly solvents up to a certain extent. Recently, volatile organic solvents have been replaced by non-volatile ionic liquid solvents possessing useful chemical and physicochemical properties. Moniruzzaman et al. (2008) successfully prepared the reverse micelles in ionic liquid ( $[\text{C}_8\text{MIM}]^+[\text{NTf}_2]^-$ ) replacing the traditional organic solvent. They suggested the possibility of forming an optically transparent aqueous nano-environment in RTILs. The explanation of aqueous droplets formation in ( $[\text{C}_8\text{MIM}]^+[\text{NTf}_2]^-$ ) was given as the hydrophobic interactions between the tail of the surfactant and the long carbon chain of ionic liquid ( $[\text{C}_8\text{MIM}]^+[\text{NTf}_2]^-$ ) and the strong tendency of the surfactant head group to interact with water. They also reported the presence of an aggregated water domain due to an insufficient amount of surfactant which was not enough to hydrate so many water molecules. Therefore, they determined the CMC of the surfactants by measuring the interfacial tension of the solutions with different concentration of surfactants. The results indicated that the surfactant aggregation in  $[\text{C}_8\text{MIM}]^+[\text{NTf}_2]^-$  differs from the surfactant aggregation in organic solvents. Similar results were presented by Anderson et al. (2003) in which they reported that the CMCs of anionic surfactant SDS and the non-ionic surfactant Brij 35 in different ILs are at higher values than those found in water, and the initial surface tensions of the neat ILs are lower than that of conventional organic solvents.

$[\text{BMIM}]^+[\text{BF}_4]^-$  ionic liquid was used as a nano-sized polar domain to prepare micro-emulsion of  $[\text{BMIM}]^+[\text{BF}_4]^-$  /TX-100/cyclohexane by Gao et al. (2004) and characterized by various techniques such as phase behavior, conductivity measurement, dynamic light scattering, freeze-fracturing electron microscopy and UV-visible techniques. In this work, the sizes and size distribution of the droplets in micro-emulsions were



characterized by dynamic light scattering (DLS) and the characterization of the size and shape of the aggregates in micro-emulsion were carried out using freeze-fracture electron microscopy (FFEM). The created nano-sized IL environment has potential applications in the synthesis of organic or inorganic materials, in carrying out a chemical reaction, and in extraction and fractionation.

Cheng et al. (2007) upgraded their work and were able to produce an emulsion of ionic liquid in another ionic liquid in which all the components were non-volatile. They prepared and characterized a micro-emulsion by using a hydrophobic ionic liquid  $[\text{BMIM}]^+[\text{PF}_6]^-$  and a hydrophilic ionic liquid propylammonium formate (PAF) with the help of surfactant AOT. They reported that the mechanism of the formation of micro-emulsion in ionic liquids is similar to that of other kind of micro-emulsions. AOT is soluble and forms micelles with hydrophobic cores of PAF, and its polar heads are led to PAF phase. The distribution of  $[\text{BMIM}]^+[\text{PF}_6]^-$  takes place in the hydrophobic groups of micelles of AOT in the PAF-rich phase. Hence,  $[\text{BMIM}]^+[\text{PF}_6]^-$  in-PAF microemulsions were obtained.

Binks et al. (2003) prepared emulsions stabilized by silica particles that were stable for up to 30 days using ionic liquids as internal/middle/outer phase. The internal drop size of the emulsion was also invariant up to 30 days against coalescence and Ostwald ripening. They found out that the emulsions containing Miglyol 810N and  $[\text{EMIM}]^+[\text{BF}_4]^-$  can undergo both transitional and catastrophic phase inversion. They also described that the volume fractions of the liquid portion and the concentrations of the silica particles somewhat provide a degree of control of the inner and outer droplet sizes. They found out that the emulsion drop size decreases upon increasing the concentration of silica nanoparticles.

Merrigan et al. (2000) reported the potential application of fluoros ionic liquids as a surfactant in another ionic liquid solvent for emulsion preparation. They formulated new types of ionic liquids derived from imidazole cations with fluoros appendage. The formulated ionic liquid was found to act as surfactants when added to other conventional ionic liquids, facilitating the emulsification. They also studied the effects of carbon chain length attached to the cation group and the chain length of fluoros tail on emulsification.

Evans (2006) reported the functionality of ionic liquids as surfactant in emulsions. He determined the stability of a fluid bi-layer in the presence of cations and anions that are in some common RTILs. The release of contents from 1,2-dielaidoylphosphatidylcholine vesicles and its size were controlled as a function of either cation or anion concentrations. It was also reported that the leakage of internal contents increases upon increasing the length of the alkyl group.

Zech et al. (2008) formulated and investigated the micro-emulsions comprising dodecane, ionic liquid surfactant  $[C_{16}MIM]^+[Cl]^-$  and RTIL: EAN and  $[BMIM]^+[BF_4]^-$ . They noticed that the prominent difference in the interfacial rigidity of the micro-emulsions was induced by changing the nature of the polar  $[C_{16}MIM]^+[Cl]^-$ , EAN and  $[BMIM]^+[BF_4]^-$ . It was confirmed by several independent techniques such as phase diagram determination, SAXS spectra treatments, conductivity, and DLS measurements.

Palladium nanowires with increased catalytic activity and stability were prepared by Gao et al. (2005) using thiol functionalized ionic liquid (1-methyl-3-(2-mercaptoacetoxyethyl) imidazolium chloride) as a stabilizer. Some hydrophobic ionic liquids have been reported to stabilize the lipase when they were co-immobilized within sol-gel derived silica (Lee et al., 2007). They also reported the usages of ionic liquids (ILs) as additives in order to protect the inactivation of enzymes by released alcohol and shrinking of gel during the sol-gel process. The activity of *Candida rugosa* lipases

immobilized by ILs was higher than that of immobilized by lipase immobilized without ILs. The hydrolytic and esterification activities with ILs were found to be 5-times and 16 times without ILs, respectively. They concluded that ILs in the sol-gel process act as a precursor during gelation and protect the enzyme from the inactivation by alcohol or heat by providing a substantial amount of stability to the enzyme. Recently, Behera et al. (2010) and Behera et al. (2009) have reported the formation of micelles and reverse micelles in IL/W (ionic liquid in water) or W/IL (water in ionic liquid), respectively. They have also demonstrated the effect of surfactant nature on micro-emulsion prepared by water and hydrophobic ionic liquids. They suggested that ionic liquids can act as both an electrolyte and a co-solvent which govern the behaviour of ionic liquids in micellar solution. They reported that the solubility of  $[\text{BMIM}]^+[\text{PF}_6]^-$  within aqueous micellar solutions increases with increasing surfactant concentration. The formation of IL-in-water microemulsions when the concentration of  $[\text{BMIM}]^+[\text{PF}_6]^-$  is above its aqueous solubility has also been suggested for nonionic TX-100 and Brij-35 aqueous surfactant solutions. However, the study on the use of ionic liquids in ELM as carrier/surfactant/stabilizers is scarce and there are only a few reports on the application of ionic liquids in emulsion liquid membrane.

In the present study, a new application of ionic liquid  $[\text{BMIM}]^+ [\text{NTf}_2]^-$  has been suggested through using another ionic liquid TOMAC as a carrier in the ELM. The role of hydrophobic ionic liquid  $[\text{BMIM}]^+ [\text{NTf}_2]^-$  as a stabilizer has been studied extensively. The ionic liquid  $[\text{BMIM}]^+ [\text{NTf}_2]^-$  was chosen due to its relatively low viscosity (52 cP) in comparison to other ionic liquids that makes the homogeneous dispersion of  $[\text{BMIM}]^+ [\text{NTf}_2]^-$  in the ELM relatively easy.