CHAPTER 2

Literature survey

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LITERATURE SURVEY

Emulsion liquid membranes, liquid surfactant membranes, liquid emulsion membranes are synonymous terms used to represent a new separation technique that originated in 1968 and has evolved since then; it is now in the process of commercialization.

A membrane is essentially a semi permeable barrier between two miscible phases. Most membranes are polymeric in nature. However, when liquid functions as a barrier between two miscible fluid phases it can also be considered as a membrane, such membranes are called liquid membranes.

An emulsion is a dispersion of one liquid in another with which it is immiscible. The two immiscible liquids that constitute an emulsion are referred to as oil and water as they are proverbial representatives of two such liquids. Within an emulsion one liquid is in the form of droplets and is therefore distinguished from the other phase. The droplet phase is often referred to as *internal phase* or *Phase I* in emulsion literature while the other phase is called *external phase* or *Phase II.* Emulsions appear as two types: Water droplets dispersed in oil designated *W/O* and oil droplets dispersed in water designated *O/W.*

When the definition of a liquid membrane is combined with that of an emulsion, the idea of an emulsion liquid membrane emerges. The Emulsion Liquid Membrane (ELM) is an emulsion working as a liquid membrane. Meaning that the external phase of the emulsion acts as a membrane separating the internal phase of the emulsion from another phase that is fully miscible with the internal phase. This can happen if the emulsion is dispersed in the bulk of a continuous phase with which its external phase is immiscible while its internal phase is miscible.

Since, the emulsions are stabilized by surfactants hence the term liquid surfactant membrane was used in the early days of the development of this technique. However, the term emulsion liquid membrane is more frequently used in current practice due to obvious reasons. In this Chapter an overview of the entire area of emulsion liquid membrane processes beginning with historical perspective is presented in *six* sections.

2.1 HISTORICAL PERSPECTIVE

N.N.Li invented the separation method based on permeation through an emulsion liquid membrane in the late sixties. This discovery stemmed out from a laboratory observation at Exxon research laboratories in USA that Saponin, a natural surfactant, forms such a strong and visible film at the oil water interface, that in a 'Du-Nuoy' ring experiment for interfacial tension, the ring could hook up the film and suspend it in the top oil phase (Li 1971a). Realizing the usefulness of this kind of instantly formed film, a separation scheme was devised for testing the feasibility of this idea.

The original separation scheme was devised to achieve separation of aromatics from paraffins which was and still remains a highly energy intensive process. The apparatus involved a small tower called a liquid membrane diffusion tower. The tower contained three phases-an aqueous surfactant solution at the bottom of the tower, a hydrocarbon solvent phase in the middle section and a raffinate solution at the top formed by the drops rising through the solvent phase. A binary feed mixture of n-hexane and benzene was bubbled through the aqueous surfactant solution from the bottom of the tower. The aqueous liquid membranes formed instantly around the drops and allowed them to rise through the solvent phase without actually dissolving in it. The solvents used had no selectivity for any of the feed components and the separation obtained was entirely due to membrane selectivity (Li 1971 b).

The solvent selected were hydrocarbons boiling well outside the range of permeate so that permeate could be separated by flash distillation. The drops after rising from the solvent phase coalesced in the top section of the column to form the raffinate phase that was analyzed for enrichment of the non-permeating feed component. Reasonably large separation factors of the order of 106 for benzene/n-hexane were obtained in single drop experiments. These findings resulted in the first patent in the area of hydrocarbon separation using liquid membranes (N.N.Li 1968).

In spite of the initial successful experiments that proved the separation scheme was workable two severe problems were encountered; partial membrane rupture leading to low overall selectivity was one of them, the other was small surface area which resulted in low overall permeation rates. Without overcoming these hurdles the liquid membrane separation technique would have remained a laboratory curiosity.

The breakthrough in this separation process was achieved when solution to these problems were found. This involved emulsifying the feed in surfactant solution that resulted in a sharp decrease of the average drop diameter from 0.5 cm to 10^{-3} cm. Both drop stability and permeation rates greatly increased owing to the tremendously increased total surface area of the drops. The emulsion thus formed was then mixed with the solvent. Varying the ratio of the emulsion to solvent did not vary the selectivity. Demulsification after emulsion solvent contact was achieved by conventional demulsification techniques.

It was quickly realized that fractionation of hydrocarbons using emulsion liquid membranes was not a very attractive proposition keeping in view the scale of separation. It was in the early 1970s that Li adopted the emulsion liquid membrane technique for removal of phenol from aqueous streams using w/o emulsions (Li and Shrier, 1972). This application became a remarkable success and since then lot of research activity has been witnessed in this area all over the world.

2.2 EMULSION LIQUID MEMBRANE SEPARATION PROCESS

Emulsion liquid membrane separation is achieved by preparing an emulsion between two immiscible phases and then dispersing the emulsion formed into a third (continuous) phase by agitation so as to extract a solute from the continuous phase into the inner phase of the emulsion or vice-versa as shown in Fig. 2.1. The membrane phase is the liquid that separates the encapsulated internal droplets within the emulsion from the external continuous phase as shown in Fig. 2.2.

When the emulsion is dispersed with mild agitation in the external continuous water phase, *Phase III,* many small globules of the emulsion are formed. The size range of these globules vary from 0.1 mm to 3mm, globule size largely depends on mode and intensity of agitation, emulsion viscosity, constituents and composition of the emulsion. A large surface area for mass transfer is generated because of the small size of the emulsion globules formed. Further the internal encapsulated droplets within the emulsion globules are just 1 to 10 μm. in diameter; that leads to an enormously large internal mass transfer area typically of the order of 10^6 m^2/m^3. The net result being that a very rapid mass transfer takes place in ELM process irrespective of the transfer being from the continuous to the inner encapsulated phase or vice-versa.

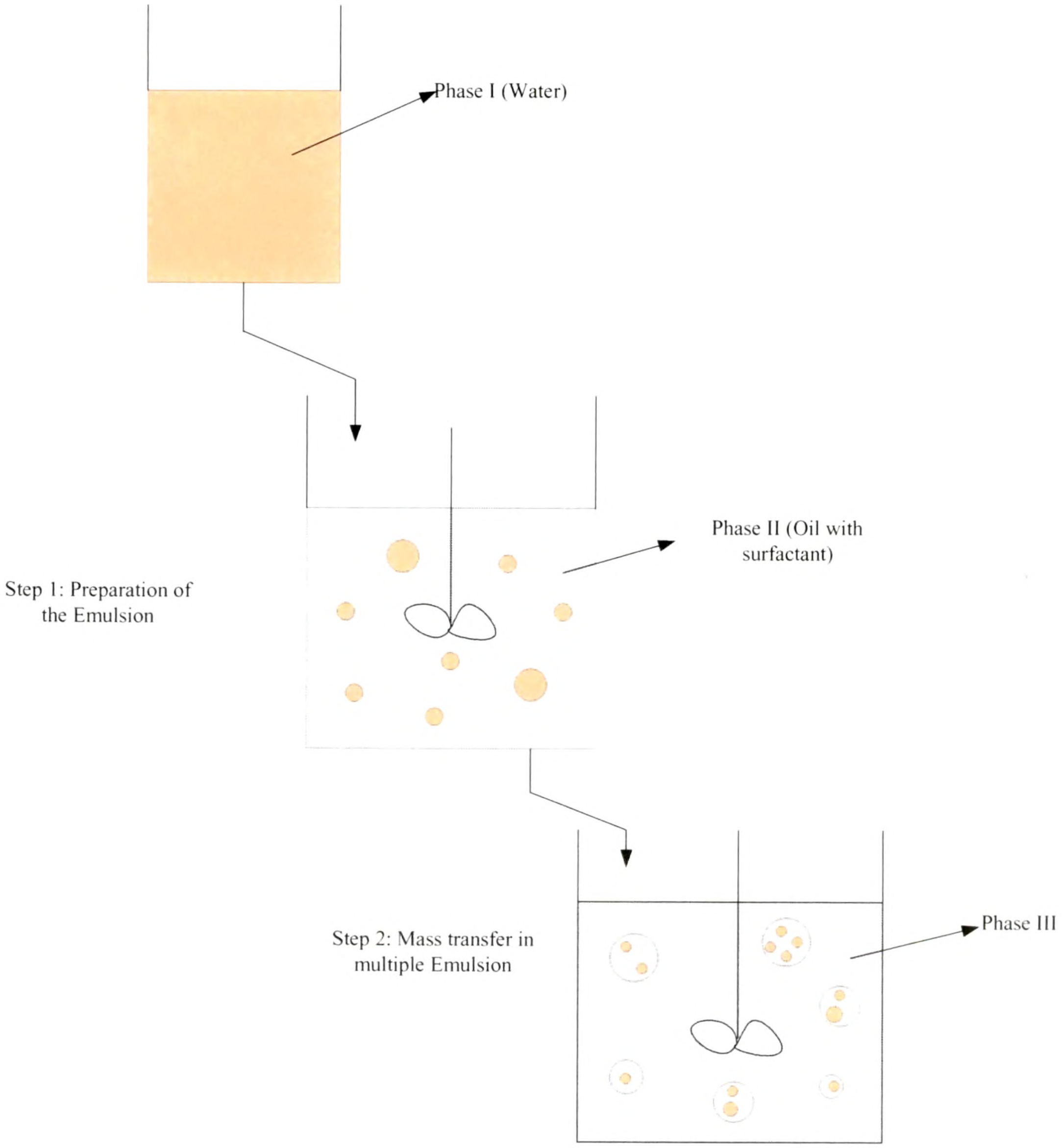

Fig. 2.1: Preparation of emulsion liquid membranes

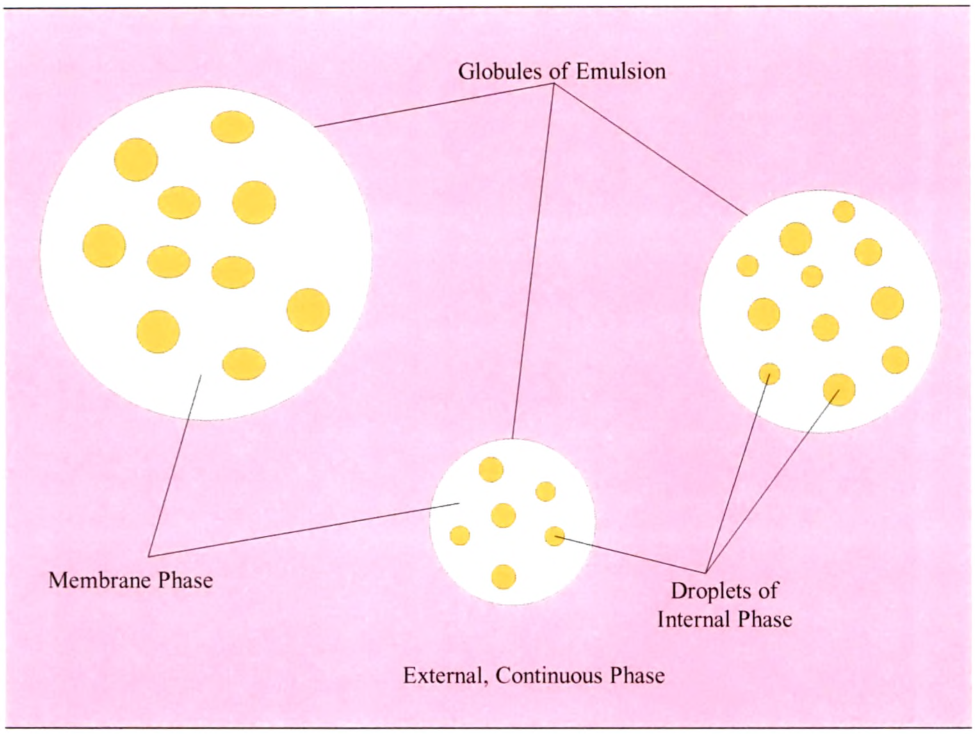

Fig. 2.2: Schematic of an emulsion liquid membrane system

Separations of mixtures are achievable by selective diffusion of one component of Phase III, through the membrane Phase II into the receiving Phase I. Surfactant/s and additive/s included in the membrane phase can control the permeability of a solute and hence the selectivity of the separation. An individual component can be trapped and/or concentrated in the internal phase of the emulsion membrane for later disposal or recovery. The overall operation can be carried out batch wise or in a continuous manner using single stage or multiple stages, with concurrent or counter current contact as the need may be.

Usually ELM processes appear to be extensively used for removal of solutes from continuous water phase using W/O emulsions. However, they are equally applicable for solute removal from organic systems using O/W emulsion. Once separation is achieved, the emulsion is separated from the continuous phase by settling. Breaking the emulsion and separating the internal phase from the membrane phase can recover the extracted component. The membrane constituents are recycled to the emulsification stage for preparation of the emulsion with a regenerated or fresh reagent phase and the process continues. Thus a continuous emulsion liquid membrane process involves four steps working in tandem; they are emulsification, emulsion dispersion in continuous phase for extraction, settling to separate the emulsion and emulsion breakage to recycle membrane components as shown in Fig. 2.3.

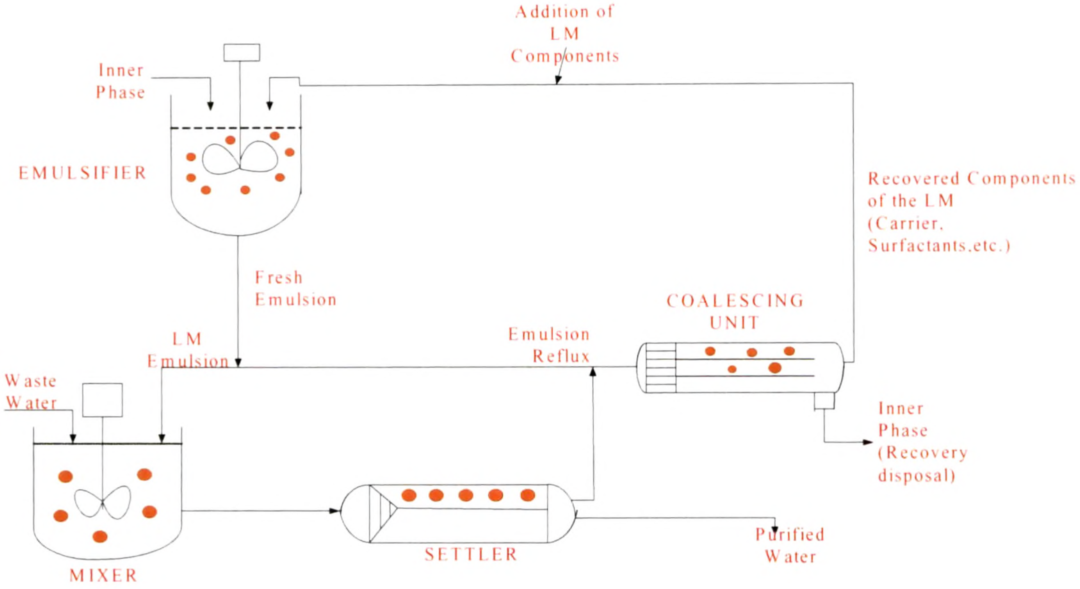

Fig. 2.3: Flowsheet of an emulsion liquid membrane process

2.3 TRANSPORT MECHANISMS INTO EMULSION LIQUID MEMBRANES

Separations using emulsion liquid membranes necessarily take advantage of the unique morphological features of such membranes wherein a membrane phase separates two miscible phases, one phase within the membrane in form of tiny dispersed droplets the other being the phase in which the emulsion itself is dispersed.

Separations are usually designed that a solute is transported from the continuous phase through the emulsion membrane and accumulated in the encapsulated tiny droplets within the emulsion. In this manner solute could be removed from a large volume of bulk phase and concentrated within the small internal phase of the emulsion.

The emulsion liquid membrane separation technique is different from solvent extraction in the sense that in ELM separation extraction and stripping takes place simultaneously in the same unit. This aspect makes the ELM technique highly attractive option for cost, energy and inventory reduction in the process industries.

An idealized concentration profile of solute 'A' permeating through an emulsion liquid membrane is shown in Fig. 2.4.

The permeation process can be divided into following five steps:

- Film diffusion through external phase boundary
- Sorption on the membrane
- Diffusion through the membrane
- Desorption from the membrane
- Film diffusion through internal phase boundary

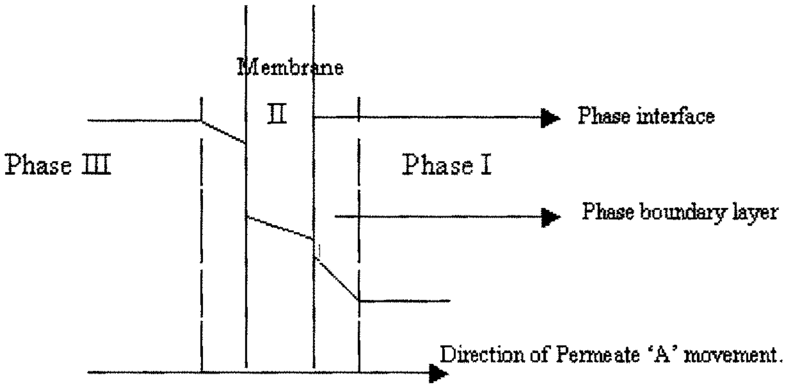

Fig. 2.4: Schematic representation of a concentration profile through an emulsion liquid membrane.

The concentration profile shown in Fig. 2.4 is obviously time dependent since an enrichment or depletion process occurs in the emulsion membrane globules. The diffusion coefficients and thickness of the membrane limit the mass transfer rates. In case of multicomponent systems, the product of diffusion coefficient and solubility of permeates in the membrane phase decisively influence the selectivity of the mass transfer process.

Permeation of a desired species from a solution into emulsion liquid membranes can take place by several mechanisms. The various solute transport mechanisms can be classified as follows (Li 1978, 1981; Kopp and Marr 1982; Ho and Li 1992)

Simple permeation: In this mechanism, permeate 'A' is soluble in the membrane and exists at different concentrations on the two sides of the membrane as shown in Fig. 2.5(a). This process is not very attractive because the transfer rates would drastically diminish with the reduction of concentration gradients. Moreover, the mass of the inner phase of the membrane is considerably less than the mass of the continuous phase therefore, no significant change of permeate concentration in the continuous phase can be expected. Simple permeation studies have been largely performed to check the stability of emulsions (Takahashi *et al.* 1981).

Simple permeation with chemical reaction: This is a significant improvement over the simple permeation mechanism. The effectiveness of the separation is significantly improved when the component to be removed (permeate A) is transformed by reaction in the receiving side to a product incapable of diffusing back through the membrane as shown in Fig. 2.5 (b). In this way there is minimization of the concentration of diffusing species in the receiving phase leading to maximization of flux and capacity. Separation of phenols, acids, bases and ammonia from wastewater are based on this scheme. Matulevicius and Li (1975) has designated this mechanism as **Type I facilitated transport.**

Simple carrier-mediated transport: In order to increase both the selectivity and mass flux, carriers are dissolved in the membrane. The carrier is soluble only in the membrane and reversibly forms a membrane soluble compound with the species to be transferred. As shown in Fig. 2.5 (c) the carrier 'C' is charged with permeate 'A' on feed side (Phase III) of solution membrane interface, the component AC diffuses through the membrane (Phase II) to the opposite phase interface (Phase II-Phase I) as a result of concentration difference and sets free 'A' on receiving side (Phase I). The carrier then diffuses back to Phase III-Phase II boundary thereby closing its circulation loop and is able to transport 'A' molecule as many times as necessary.

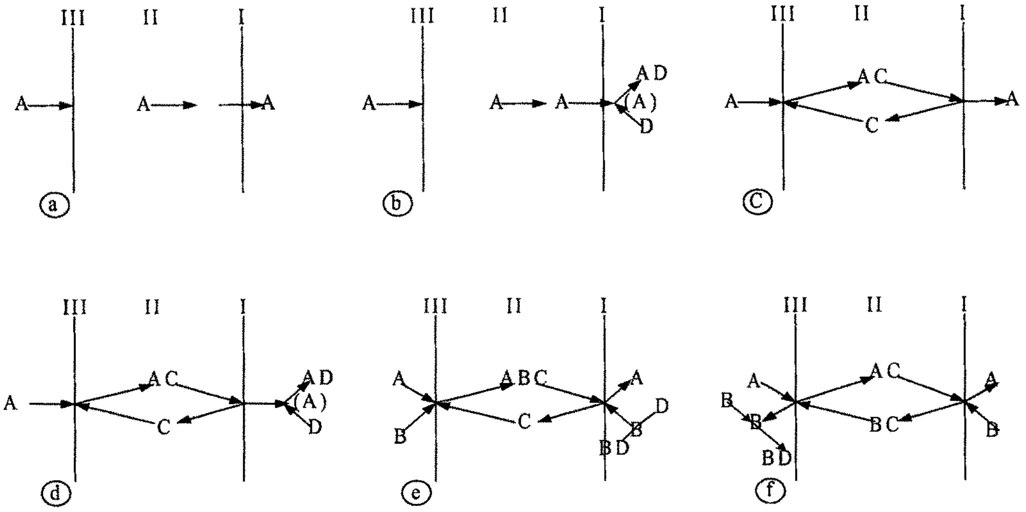

Fig. 2.5: Transport mechanisms of liquid membrane permeation

The carrier increases the solubility of 'A' in the membrane material; as a result increased permeation rates are possible. The transport of 'A' is no longer a function only of the gradient of 'A' but also depends on the concentration of the carrier. The transport process comes to an end when an equality of the concentration of 'A' prevails on both sides of the membrane. This type of transport is often referred to as **facilitated diffusion**.

Carrier-mediated transport with a chemical reaction on the receiving side: In this mechanism the permeate 'A' reacts with an reagent 'D' in the receiving phase after it gets dissociated from the carrier in the receiving phase/ membrane interface as shown in Fig. 2.5 (d). It is necessary that the new species 'AD' formed in the receiving phase must be non-permeating. Coupled transport is a special case of such carrier-mediated transport with reaction, here the interactions between permeate species and carrier is an ion exchange reaction.

In case of coupled transport, the membrane contains a carrier that can lead to transport of permeate only when two different species, one being the desired permeate, present themselves at the same time. If transport of the two species occurs in the same direction its called co-transport while if they occur in opposite directions it is called counter transport. Li and coworkers (1975,1981 and 1992) designated carrier-mediated transport with chemical reaction as **Type II facilitated transport.**

Co-transport: Targeted permeate 'A' and species 'B' are transported in one direction and the uncharged carrier 'C' diffuses back as shown in Fig. 2.5(e). If 'B' is present in excess in feed (Phase III), 'A' can still be transported through the membrane even when the concentration of 'A' in the receiving phase (Phase I) is larger than the feed side. The concentration of 'B' can be brought down to zero in the receiving phase using an auxiliary chemical reaction then 'A' can be transported almost quantitatively from the feed side to the receiving side. The driving force is the concentration difference of 'B'. This process of transporting mass against its gradient is called **'pumping'**. This transport mechanism is particularly used for transport of metal anions from feed to receiving phase using basic carriers.

Counter transport: As the name implies the targeted species 'A' is transported within the emulsion liquid membrane with help of 'B' that is transported in the opposite direction as shown in Fig. 2.5 (f). The following steps occur during this process:

- 'A' diffuses to the membrane and reacts with 'BC', as a result of which 'B' is liberated and the carrier complex 'AC' charged with 'A' is formed;
- 'AC' diffuses to the other side of the membrane;
- 'AC' reacts with 'B' to form 'BC' as a result of which 'A' is liberated on the receiving side III;
- 'BC' diffuses from side III to side I, and this way the carrier cycle is completed. An excess of 'B' leads to complete separation of 'A' on side I.

The transport of bivalent transition metal cations, that are considered to be among the most attractive applications of emulsion liquid technique, happen to follow this mechanism and have been widely investigated.

2.4 ESSENTIAL FEATURES OF EMULSION LIQUID MEMBRANES (ELMs)

The ELM process essentially consists of four steps:

- Emulsification
- Dispersion of the emulsion in the bulk of continuous phase
- Separation of the emulsion from the external phase by settling after extraction
- Breakup of emulsion to recover the internal phase as extract with subsequent recycle of the membrane phase constituents.

The technical success of the ELM process largely depends on the first two steps however all steps are of importance for the commercial success of the process. The emulsion is the heart of the process hence the overall success of the process depends on the nature of the emulsion, its constituents, its formulation, morphology and its stability.

Emulsion Types: Emulsions are either Water in Oil type (W/O) or Oil in Water type (O/W), they are formed by mixing immiscible liquids viz. water and an organic liquid under conditions of high shear in the presence of emulsifiers. The phase in which the emulsifier dissolves becomes the external phase of the emulsion.

If the emulsifier is lipophilic in nature it dissolves readily in the oil phase, reducing the surface tension of the oil imparting it greater spread ability resulting in formation of W/O emulsion. If the emulsifier is hydrophilic it dissolves in water phase resulting in O/W emulsions. Thus by selecting an appropriate emulsifier W/O or O/W emulsions can be obtained from any oil phase in contact with water phase.

2.4.1 Membrane Materials

Emulsion liquid membrane separations usually involve situations wherein organic or metal solutes are separated from aqueous streams using W/O emulsions. The external phase of such emulsions is essentially organic in nature, immiscible with water and function as the liquid membrane. Membrane materials may be either hydrocarbon fractions or pure hydrocarbon solvents such as hexane, decane etc. The emulsifier and the carriers (extractants used for type II separations) are dissolved in the membrane phase.

Ideal membrane material should posses the following properties (Gu, Ho & Li 1992)

- Be compatible with carrier and surfactant without formation of the new phases.
- Have low solubility in the internal and external aqueous phases to minimize the solvent loss.
- Have a moderate viscosity.
- Have sufficient density difference from the aqueous phase for rapid settling.
- Be both cheap and readily available.
- Have low toxicity and high flash point for safety reasons.

Based on these considerations aliphatic hydrocarbons are preferred over aromatic hydrocarbons since they meet most of the above listed requirements. On the whole it is observed that the membrane materials used to formulate emulsion liquid membranes can be classified in the following four categories:

Proprietary Solvents: Most extensively used solvents in this category are the following: -

> **S100 N ®**: Exxon's 'Solvent 100 Neutral' is a dewaxed isoparaffinic middle distillate having molecular weight 386.5, pour point 32.2 and specific gravity 0.85 at 25°C. Pioneering investigators Li and Shrier (1972), Li, Cahn and Shrier (1973), Cahn and Li (1974), Terry, Li and Ho (1982), Ho *et al.* (1982) used ELMs formulated from S100 N for phenol removal from aqueous streams. Kitagawa *et al.* (1977) and Frankenfeld *et al.* (1981) used S100 N based ELMs for removal of mercury and copper from waste streams respectively. Downs and Li (1981) used S100 N membranes for ammonia extraction from municipal wastewaters.
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> **LOPS ®:** Exxon's 'Low odor paraffin solvent' typically contains 52% paraffin, 45% napthenes and 3% aromatics. It has an average molecular weight of 180 and specific gravity of 0.796 at 15.6°C. Terry, Li and Ho (1982) used LOPS membrane for the extraction of phenol and acetic acid from aqueous streams. Hayworth (1983) extracted uranium from phosphoric acids using ELMs with LOPS as membrane material. Gu, Wasan and Li (1985) used

LOPS as membrane material to extract cobalt, nickel and copper from water streams into ELMs.

Shellsol T ®: It is a paraffinic solvent containing less than 0.5% aromatics from Shell. Draxler and Marr (1986) formulated emulsion membranes from Shellsol T to extract nickel from electroplating solutions. Kakoi *et al.* (1996) and Kataoka *et al.* (1997) reported extraction of phenols from aqueous streams using membranes made from Shellsol. Abou-Nemeh and Van Peteghem (1993) used Shellsol membranes for cobalt extraction.

Reis *et al.* (1993, 2004) reported zinc extraction using ELMs formulated from Shellsol. Further Shellsol T is used as the membrane material in the commercial extraction of zinc from wastewaters of viscose fiber plants using emulsion liquid membranes (Marr and Draxler 1992).

Petroleum fractions and derivatives:

Kerosene: Kerosene has emerged as the membrane material of choice of most investigators in recent years. Preference for kerosene stems from its ease of availability, low cost, low viscosity and good miscibility with emulsifiers and carriers. Many commercially used carriers (metal extractants) are marketed dissolved in kerosene.

Emulsion liquid membranes formulated using kerosene as membrane phase were used to separate the following solutes from aqueous streams: - copper: (Volkel *et al.* 1980); phenol: (Chang and Li 1983, Teramoto *et al.* 1983, Zhang Liu and Lu 1987); vanadium: (Zheng *et al.* 1988); rare earths: (Zhang and Wang 1989); cobalt: (Strezelbicki and Schlosser 1989); molybdenum: (Hirato et al.1990); strontium: (Eroglu *et al.* 1993); uranium: (Hirato 1991,.El Sayed 2003); Penicillin G: (Lee and coworkers 1992, 1997 and 1998); phenylalanine : (Liu and Liu 1998) ; cadmium: (Urtiaga *et al.* 2000); chromium VI : (Banerjea *et al.* 2000 and Bhowal & Dutta 2001); nickel : (Chakraborty *et al.* 2003).

Liquid Paraffin: ELMs formulated from liquid paraffin were used by Yagodin *et al.*(1983) to extract cholesterol from blood. Fudu *et al.* (1985) extracted phenol from waste waters into paraffin based ELMs. Bart *et al.* (1992) used n Alkane C_7 – C_{12} for zinc extraction from aqueous streams. Chromium VI was extracted by Chakravarti *et al.* (1995) from wastewaters into ELMs having liquid paraffin as the membrane phase. In recent years ELMs with liquid paraffin as membrane phase was used by Sznejer and Marmur (1999) for cadmium removal, Kulkarni *et al.* (2002) for uranium removal and Kargari *et al.* (2004) for gold removal from aqueous streams.

Pure Solvents: Pure solvents have also been used by a number of workers for emulsion membrane formulation. ELMs formulated from n-heptane was used by Goto *et al.* for the extraction of zinc (1991) and rare earths (1993): Juang and Jiang (1995) for extraction of nickel and Kasani *et al.* (1998) for extraction of cobalt.

Lee, Wang and Wang (1994) used n- dodecane as membrane phase for extraction of trivalent europium. Li (Quanmin) *et al.* (1997,1998) using ELMs made from o-Xylene and dimethyl benzene respectively, removed cadmium from aqueous solutions. Larson, Raghuraman and Wineck (1994) extracted mercury from wastewater streams into ELMs made from tetradecane. Solanki and Sengupta (2003) used toluene membranes to extract phenol from aqueous streams.

Mixed Solvents: Mixed solvents have also been used to formulate W/O emulsions for emulsion liquid membrane extraction. Kataoka *et al.* (1989) used kerosene - liquid paraffin mixtures as membrane phase for phenol extraction. Gadekar *et al.* (1992) separated nitrophenols using kerosene and paraffin membranes. Yang *et al.* (1996) used kerosene – heptane blends in ELMs to extract copper, chromium, zinc and mercury from waste streams. Li (Longquan) (1997) used kerosene – liquid paraffin membranes for the separation of cobalt and nickel from aqueous streams. Chakravarti *et al.* (2000) also used kerosene – liquid paraffin blends for copper removal from aqueous streams. Kulkarni and Mahajani (2002) used membranes made of kerosene blended with xylene, dodecane and heptane respectively to extract molybdenum from aqueous streams. Kumaresan *et al.* (2003) used xylene – liquid paraffin membranes for treatment of distillery wastes. In all of the above mentioned investigations the rationale of using mixed solvents is to get a membrane phase with enhanced aliphatic content.

2.4.2 Surfactants:

Surfactant is the key component for forming a stable emulsion. With reference to the W/O emulsions extensively used in emulsion liquid membrane separations, an ideal emulsifier for these emulsions should posses the following properties (Gu, Ho and Li 1992).

- It should be soluble in the membrane phase but insoluble in both the internal as well as the external aqueous phases.
- It should be stable against acids, bases and bacteria.
- It should not react with the carrier (extractant) in the membrane phase.
- It should not facilitate water transport into the emulsion during operation so as to alleviate osmotic swelling.
- It should have low interfacial resistance to mass transfer.
- It should not inhibit demulsification.
- It should be cheap and non-toxic for economic and environmental considerations.

Very few attempts have been made to design and synthesize surfactants for ELM applications. The most widely used surfactant for preparing W/O emulsions, for ELMs, is Sorbitan monooleate (Span 80 ®). Polyamine surfactants and its derivatives are also frequently used for preparing ELMs.

Sorbitan monooleate is a nonionic surfactant having Mol. Wt = 428 and HLB = 4.2. Commercially it is the most easily available and widely used surfactant to prepare W/O emulsions. Span 80 is a fairly good emulsifier; emulsion membranes prepared from Span 80 show low resistance to mass transfer in comparison with other surfactants (Draxler and Marr 1986, Strzelbicki and Schlosser 1989, Lee and Chan 1990). However it suffers from some draw backs, emulsions prepared using Span 80 are prone to osmotic swelling (Martin and Davies 1977, Colinart *et al.* 1984, Draxler and Marr 1986, Nakashio *et al.* 1988, Hirato *et al.* 1990, Abou-Nemeh and Van

Peteghem 1990). Emulsions prepared with Span 80 are not very stable under highly alkaline conditions (Zhang 1988, Abou-Nemeh *et al.* 1990, 1992, 1993).

Abou-Nemeh *et al.* (1990) postulated that the reason for instability of Span 80 based W/O emulsions with inner alkaline phase could be due to the hydrolysis of the ester linkages of the emulsifier. However, their experimental findings reveal that the hydrolysis of Span 80 in kerosene media is extremely slow. Mikucki and Osseo-Asare (1986) reported that Span 80 causes a decrease in the rate of interfacial chemical reactions by its preferential adsorption at the interfaces of the emulsion globules and showed that an optimum surfactant concentration exists in copper extraction with an ELM containing LIX 64 N and Span 80. Pilot plant investigations by Ruppert, Draxler and Marr (1988) reveal that bacteria could destroy Span 80.

Nonionic polyamine surfactant ECA 4360 (MW = 1800) and its derivatives are reported to form more stable emulsions in comparison to Span 80 (Goto et. al. 1987, Qian, Ma and Shi 1989), cause less osmotic swelling (Nakashio *et al.* 1988) and are sparingly soluble in water (Draxler, Furst and Marr 1988, Zhang and Xiao 1989 and 1990). However, these emulsifiers show poor stability with organic and inorganic acids (Draxler and Marr 1986, Zhang *et al.* 1988). Another drawback of ECA 4360 is its high resistance to interfacial mass transfer (Wasan, Gu and Li 1984, Strezelbicki and Schlosser 1984). In cases of carrier mediated transport ECA 4360 is reported to enhance the decomposition of the carrier. (Draxler and Marr 1986).

Some investigators noted that using combination of surfactants might be a remedy to overcome the shortcomings of sorbitol esters and polyamine surfactants. Draxler and Marr (1986) showed that adding Span 80 to ECA 4360 reduced the mass transfer resistance and kept the swelling to a tolerant level. Similarly Zhang and Wang (1989) improved membrane stability and extraction efficiency by using a mixture of Span 80 and polyamine surfactants.

Some surfactants have synergistic effects with extractants. Miyake *et al.* (1983) found that extraction rate with SME 529 was accelerated by anionic surfactants. Zhang *et al.* (1989, 1990) observed that polyamine surfactant N 205 enhanced the extraction of rare earths.

Nakashio and coworkers have synthesized two new types of surfactants both of which have two long alkyl chains (Goto *et al.* 1987). One is a series of derivatives of nonionic glutamic acid dialkyl esters abbreviated as 2RGE, and the other is a series of derivatives of cationic quaternary ammonium salts abbreviated as 2R'QA. Their experiments on copper extraction with LIX 65 N showed that Glutamic acid derivatives were better surfactants than SPAN 80 and ECA 4360 with respect to membrane stability, swelling, extraction rate and demulsification (Nakashio *et al.* 1988). Investigations on zinc extraction by these investigators show that synthesized surfactants having two oleyl chains form a stable emulsion in an even lower concentration range than do the commercial surfactants. They also found that the extraction rate was strongly affected by the surfactants, and the cationic surfactant accelerated the extraction rate of zinc due to electrostatic interaction with the carrier PC-88A (Goto *et al.* 1991).

Goto *et al.* (1993), Nakashio (1993) also extracted rare earth metals lanthanum, praseodymium and neodymium into liquid emulsion membranes formulated using nonionic dioleyl $_{\text{L}}$-glutamate ribitol and cationic dioleyl $_{\text{L}}$-glutamate quaternary ammonium chloride. These investigators have reported the overall rate constants for the above-mentioned surfactants also for emulsion membranes formulated from Span 80 and polyamine PX 100. It was observed that the cationic surfactant accelerated the extraction rate of rare earth metals and showed the best result in all separations while the extraction rates with the other three surfactants were comparable.

Zhang *et al.* (1988) synthesized surfactant LMS-2 a copolymeric anionic surfactant containing C_4 alkene groups. They report that LMS-2 form stable emulsions with minimum swelling and is suitable for encapsulating both acid and bases. Emulsions formed with LMS-2 could be demulsified by electrostatic coalescence and the surfactant is compatible with acidic basic and neutral extractants. Lui, Zhang and Fan (1990) on the basis of LMS-2 synthesized EM 301 a sulfonic acid type anionic surfactant, they report that this surfactant is comparable to LMS-2. Liu *et al.* (1995) report that surfactant LYG-G2 (sulfonated polybutadiene) showed better emulsion stability than ECA 4360 and EM –301 for aqueous HCl feeds.

Wan et al,(2001) developed polyamine surfactant LMA a copolymer of isobutene and isoprene in hydrophobic sites and polyethylene and polyamine in hydrophilic sites. Suitable surfactants are those having number average molecular weight in the range of 5000 to 9000, these surfactants are reported to exhibit higher stability, low swelling ratio, and greater resistance to strong acids and bases in comparison with Span 80 and commercial available polyamine surfactants. Kargari *et al.* (2004) used a biodegradable emulsifier for the first time in ELM technology. However, pilot plant investigations by Ruppert, Draxler and Marr (1988) reveal that bacteria could also destroy Span 80.

In an attempt to correlate membrane swelling behaviour with surfactant properties Ding *et al.* (1991) estimated the area occupied by each surfactant molecule and calculated the dipole moment for each monolayer for several surfactants such as LMS-2, EM-301, Span 80, polyamines. They found that the surfactants that offer small membrane swelling such as LMS-2 and EM-301, exhibited high values of both occupied areas and dipole moments.

There is a continuous search for superior surfactants in ELM processes to fulfill the demands put on the surfactants in ELM processes. Therefore, results obtained by Ding and coworkers provide interesting information for screening and synthesizing surfactants for improving emulsion liquid membranes.

2.4.3 Emulsion preparation:

A stable emulsion that avoids any loss of emulsified droplets is an essential requirement for the ELM separation process. Stable emulsions require that the mean diameter of the internal phase droplets should be small typically in the range of 1-5μm and to fulfill this condition a high input of energy to the water oil system needs to be provided for emulsification.

Walstra (1983) has discussed various methods and devices to produce emulsions. In laboratory studies emulsions are prepared using either high-speed agitators rotating at speeds up to 5000 rpm (Chan and Li 1974, Kim *et al.* 1983, Kulkarni *et al.* 2001, Chakraborti *et al.* 2003) or Waring blenders rotating at 10,000 to 20,000 rpm (Ho *et al.*1982, Terry *et al.* 1982, O'Brien and Senske 1989, Liu and Liu 1998).

Ultrasonic homogenizers have also been used by investigators such as Teramoto *et al.* (1983), Goto and coworkers (1991, 1993 and 1996) for formation of W/O emulsions. Shere and Cheung (1988a, 1988b) report that emulsions prepared by ultrasonic emulsifiers are very stable. Teramoto *et al.* (1983) compared direct sonication with indirect sonication methods and observed that indirect sonication could be continued for longer periods of time which was not possible with direct sonication method due to intense heat release at contact parts. Further they observed that internal droplet sizes reduced to much smaller sizes with indirect sonication with longer time interval in comparison with direct sonication with shorter time intervals.

Commercial scale emulsification equipment involve colloid mills and Ultraturrax homogenizers both are rotor stator devices having very small slit widths and are designed to achieve very high shear rates (10^7 s^{-1}). Zhang *et al.* (1987) used colloid mills to prepare their emulsions. Ultraturrax homogenizers have been used more widely than colloid mills in ELM studies Abou-Nemeh and Van Peteghem (1993), Bart *et al.*(1995), Kasani *et al.*(1998), Reis *et al.*(1993, 2004), Urtiaga *et al.* (2000) and M.El Saiyed (2004) used this device to prepare W/O emulsions for ELM separations.

High-pressure homogenizer is the equipment of choice for continuous scale operations when very narrow size distribution of inner droplets are desired. This device works at pressures of 10 to 40 Mpa, generated by a positive displacement pump that forces the emulsion forming fluids through a narrow valve slit (typically 0.1 mm). The valve opens against a spring and the released fluid gains high momentum converting potential energy to kinetic energy, turbulence and cavitation in the fluid phase breaks the inner phase into very tiny droplets that get coated by the membrane phase. This device works with very high energy densities of the order of 10^{12} W/m^3.

Often in ELM processes the stripping phases are highly acidic leading to severe corrosion problems in high-pressure homogenizers as well as in rotor stator devices.

Marr *et al.* (1988, 1990) addressed this problem by designing and fabricating a static homogenizer that was employed for emulsion preparation on commercial scale for removal of zinc from wastewater in the viscose industry.

2.4.4 *Emulsion stability:*

Emulsion is a construct; it is an artificial entity, often stabilized by surfactants. Emulsion stability can therefore be related to the time span the emulsion sustains itself without separating into its constituent phases. Fig. 2.6 shows the ultimate fates of emulsion related to emulsion stability. Tadros and Vincent (1983) list five ways in which the structure of a dispersion of liquid droplets in a continuous liquid medium can change. They are as follows:

- No change in droplet size or distribution, but buildup of an equilibrium droplet concentration gradient within the emulsion. The result is a close packed array of droplets at one end of the system with remainder volume occupied by the continuous phase liquid. This phenomena results from external force field usually gravitational, centrifugal etc. acting on the system. Creaming is a special case in which the droplets collect in a concentrated layer in the top of the emulsion as shown in Fig. 2.6.
- Basic droplet size of the emulsion does not change but there is buildup of aggregates of the droplets within the emulsion. This process is known as flocculation and results from the existence of attractive forces between the droplets as shown in Fig. 2.6.
- Flocculated droplets in an aggregate in the bulk of an emulsion or droplets resulting from creaming coalesce to form larger droplets. This results in a change in the initial droplet size distribution and eventually leads to complete segregation of emulsion into two immiscible bulk liquids.
- The average droplet size in the emulsion can increase, without droplet coalescing, occurs if the two liquids forming the dispersed and continuous phases are not totally immiscible. If emulsion is truly mono disperse then no effect arising from this mutual solubility will arise. However if emulsion is polydisperse, larger droplets will form at the expense of smaller droplets owing to Ostwald ripening.

- Emulsion may invert i.e. an O/W emulsion may change to W/O emulsion. This may be brought about by a change in temperature or concentration of one of the components or addition of a new component to the system.

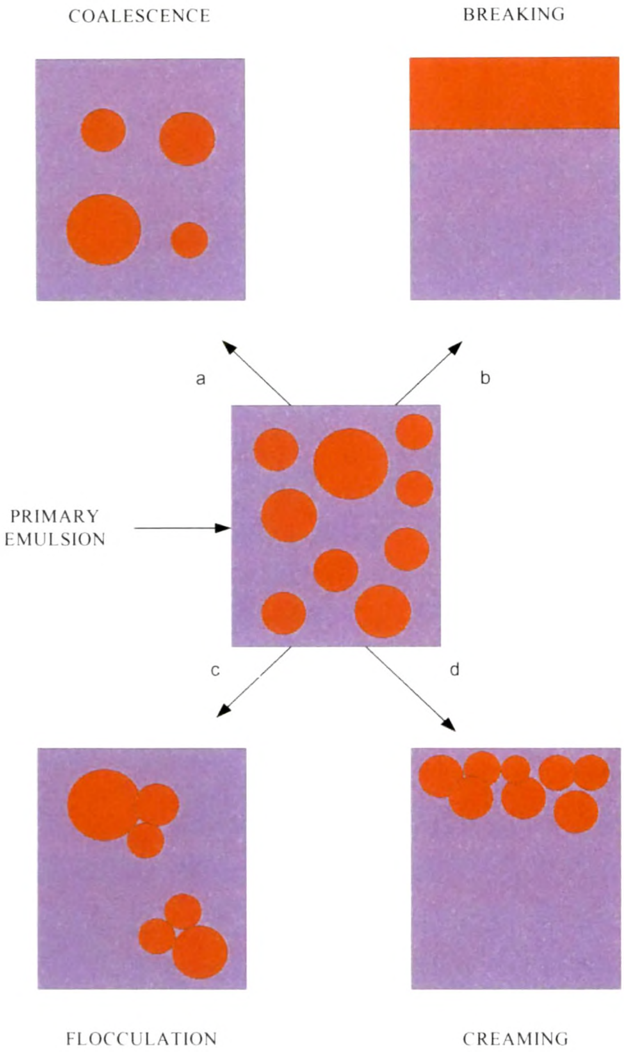


Fig.2.6: The ultimate fates of emulsions related to colloidal stability

The objective of a designer would be to formulate an emulsion that would retain its identity and remain stable as long as the emulsion process continues and which could also be quickly and effectively demulsified to recover its membrane phase for reuse.

Process variables that influence the stability of emulsions are nature and concentration of surfactants, viscosity of phases, the volume fraction of dispersed phase. The way substances are added can also have a bearing on the stability of emulsions particularly in the laboratory scale, adding disperse phase slowly to the continuous phase during emulsification is often advantageous.

In general, the higher the surfactant concentration, the greater the miscibility of surfactant in the membrane phase, and the lower the solubility of the membrane in the aqueous phase, the higher the oil viscosity, greater intensity and time of agitation lead to a reasonable stable W/O emulsion

It must be noted that all rules stated above have exceptions. There does not exist any unique set of rules to ensure formation of stable emulsions. Most information is heuristic in nature. The state of knowledge about emulsion and emulsification in spite of intensive research done in this area remains inconclusive and thereby justifies the statement often made 'Emulsion formation is an Art.'

2.4.5 Emulsion dispersion techniques:

Emulsion liquid membranes are dispersed by agitation in the continuous phase containing targeted solute. Many small globules of the emulsion get formed in the continuous phase. Globule sizes range from 0.1mm to 2mm in diameter, each globule in turn contains many tiny encapsulated droplets of 1 to 50 μm in diameter. The large surface area generated expedites the process of solute removal from continuous phase and its entrapment in the inner phase of the emulsion.

Contacting the ELM with the continuous phase can be done batch wise or in continuous manner. Batch operations are normally performed in the laboratory scale experiments designed to screen membrane materials and surfactants, studying factors influencing membrane stability, evaluating mass transfer rates and elucidating mass transfer mechanisms. Batch experiments are useful for assessing overall feasibility of the operations and optimizing the numerous process variables and acquiring the basic data necessary for scale up.

Continuous operations using ELMs are carried out in mixer-settlers or column extractors. Li and Shrier (1972) were the first to report the performance of two-stage continuous operation for phenol removal from wastewater streams. Downs and Li (1981) studied ammonia removal from municipal wastewaters in a two-stage mixer settler assembly. Mixer settler offers considerable flexibility in terms of only slow changes in performance with phase flow ratio and rates thus allowing adoption to changing feed compositions. Their drawbacks are large equipment size and potential loss of reagents. Kitagawa *et al.* (1977) and Hayworth *et al.* (1983) are other notable investigators who studied continuous extraction into ELMs using mixer-settlers.

Column contactors are compact and efficient devices that are more suitable for large-scale extractions than mixer-settlers. Cahn and Li (1981) used stirred counter-current columns for phenol extraction into ELMs and reported problems caused by foaming at interfaces of continuous and dispersed emulsion phase in the column. Bart *et al.* (1988) extracted copper ions into emulsion liquid membranes on a continuous scale using a 6m high and 0.1m -diameter column.

Mok *et al.* (1996, 1997) studied the extraction of Penicillin-G with ELMs in multi-stage counter-current mixing columns. Lee *et al.* (19970 used the Oldshue- Rushton multi-stage mixer column for extraction of Penicillin-G into ELMs. In recent years Kumaresan *et al.* (2003) treated distillery effluent with ELMs in York- Schiebel columns at optimized experimental conditions obtained from batch operations. They found the extent of BOD and COD removal almost identical in batch and continuous operations and recommend the York-Schiebel column for largescale operations.

Multi-stage operations using ELMs however, may suffer from serious emulsion swelling problems caused by the entrainment of water from external phase to the internal phase due to repeated dispersion and coalescence of emulsion globules as reported by Ma and Shi (1987).

2.4.5.1 Emulsion Globule Size and its Prediction:

Size of emulsion globules determines the mass transfer surface area between the emulsion and external phase for given volume of emulsion dispersed in a continuous media. Size of globules depends on the viscosity of the emulsion, characteristics and concentration of the surfactant in the emulsion and the mode and intensity of mixing in the dispersion operation. Teramoto *et al.* (1983a, 1983b) showed that the Sauter mean diameter was sufficient to characterize the globule size and it was not necessary to use the size distribution.

Ho, developed a dynamic technique that uses the Fraunhofer diffraction principle for measurement of emulsion globule size in a mixer with a marine propeller. He found that controlling viscosity was the viscosity of the emulsion and not the membrane phase viscosity. Further he observed that the globule size increased with increasing emulsion viscosity for a given impeller tip speed and the Sauter mean diameter correlated well with the impeller tip speed. Moreover, Ho also found insignificant effect of hold up of emulsion and the number of impellers on globule size which suggests insignificant coalescence of emulsion globules (Gu, Ho and Li 1982).

Ohtake *et al.* (1987) investigated the effects of modes of mixing on the entrainment of the external phase of water into emulsion globules and size of globules. These investigators used two modes of mixing in the first case the emulsion was settled on the water layer before stirring and in the second case the emulsion was added drop wise into the center of the external phase during stirring. The first mode of mixing gave entrainment as high as 5-30%, much more than the second mode. They developed a correlation to predict the Sauter mean diameter as a function of Weber number and viscosity of the emulsion for the second mode of mixing.

Zhou and Kresta (1998) presented a comprehensive review for mean drop size correlations in liquid-liquid dispersions. Their review did not account for a single correlation of emulsion dispersions. Emulsion dispersions are difficult to model because they are subjected to number of non-idealities such as emulsion swelling, rupture and non-Newtonian behaviour. There exist in literature few correlations to predict mean globule sizes for emulsion dispersions. These equations are listed in Table 2.1.

The diversity of the correlations reflects the scope of the problem. The differences among the correlations have their roots in the techniques adopted for droplet size measurement and also the phase selected to represent the effect of dispersed phase viscosity in the correlations.

Kataoka and Nishiki (1986) obtained three different correlations depending on surfactant used to stabilize the emulsion, presence of carrier etc. These investigators considered the dispersed phase viscosity as the membrane viscosity. Ohtake *et al.* (1987), and Sharma *et al.*(1991) used the viscosity of the emulsion as the dispersed phase viscosity. Further, Ohtake *et al.* reported that the emulsion studied was non-Newtonian in nature while Sharma *et al.* report the emulsions studied by them to be Newtonian in nature.

Rautenbach and Machhammer (1988) also developed a correlation to predict d_{32} for dispersion of ELMs in stirred vessels equipped with six bladed turbine. Their correlation uses the emulsion viscosity; they also provide a correlation to evaluate the emulsion viscosity in terms of membrane phase viscosity, density and internal phase volume fraction of the emulsion that could be utilized in case emulsion viscosities are not measured.

Table 2.1: Emulsion globule size correlations

Reference	Correlation	Conditions
Katoka and Nishiki (1986)	$d_{32}/ d_I = 0.016[We (\Delta\rho /\rho_2)(\mu_1/ \mu_2)]^{-0.375}$ $d_{32}/ d_I = 0.012[We (\Delta\rho /\rho_2)(\mu_1/ \mu_2)]^{-0.22}$ $d_{32}/ d_I = 0.066 [We (\Delta\rho /\rho_2)(\mu_1/ \mu_2)]^{-0.75}$ (In above equations the subscripts 1 and 2 represents oil phase and continuous phase respectively)	No carrier, no solute transfer, no swelling. Carrier, solute transfer with swelling. Carrier, solute transfer, no swelling
Ohtake et al. (1987)	$d_{32}/ d_I = 0.12\ We^{-0.5}$ $d_{32}/ d_I = 0.12\ \mu_e * 0.8\ We^{-0.5}$ μ_e is emulsion viscosity	$\mu_e < 0.16$ Ns/m^2 $\mu_e > 0.16$ Ns/m^2 up to 30 % swelling
Rautenbach and Machhammer (1988)	$d_{32}/ d_I = 0.11 (\eta\rho_e / \eta_e \rho)^{0.32} We^{0.7} [(V_m + V_i) /(V_m + V_i +V_e)]^{0.1}$ For emulsion: - $(\eta / \rho) = (\eta_m / \rho_m) \exp[5.32\{(V_i/ V_m+V_i)-0.1\}]$ (subscripts i, m, e represent internal phase, membrane phase and emulsion respectively)	
Sharma et al. (1991)	$d_{32}/d_o = (1 + B N_{vi})^{0.6}$ $d_o = C_1 (1 + a_1\phi_1)^{1.2} (1 + a_2\phi_2)^{1.2} We^{-0.6} d_I$ $N_{vi} = (\rho_c/ \rho_d)^{0.5} [\{(\mu_d\, \varepsilon^{-1/3} d_{32}^{1/3})/\sigma \} (1 + a_1\phi_1)^{-1} (1 + a_2\phi_2)^{-1}]$ (Subscripts c, d represent continuous and dispersed phases respectively. B, C_1, a_1 and a_2 are constants)	0.11Ns/m^2 < μ_e < 0.16 Ns/m^2 $\phi_1 = 0.32, 0.5, 0.58$ $\phi_2 = 0.05, 0.025$;
Gallego–Lizon et al. (2000)	$d_{32}{}^0/ d_I = 0.75\ We^{-0.6} (\phi)^{0.136}(\mu_e / \mu_c)^{0.11} [1 - F^{\delta w}]^{1/3}$ $F^{\delta w} = (d_{32}{}^3 - (d^0{}_{32})^3) / (d^0{}_{32})^3$ (Subscripts c and e represent the continuous and emulsion phase respectively)	

[Nomenclature for Table 2.1: d_{32} = Sauter mean diameter, d_I = diameter of impeller, d_o = drop diameter inviscid drop, $d_{32}{}^0$ = Sauter mean diameter at zero swelling, We = Weber number, ϕ, ϕ_1 = volume fraction of internal phase in the emulsion, ϕ_2 = volume fraction of dispersed phase]

In recent years Gallego-Lizon and Perez de Ortiz (2000) conducted an extensive study on drop sizes in liquid membrane dispersions using endoscopic techniques. These investigators studied the effect of emulsion swelling and shear dependent emulsion viscosity on mean emulsion globule size in addition to the effect of stirring speed and internal phase volume fraction of emulsions made from low order kerosene membranes containing extractant CYANEX 302® and emulsifier Arlacel C. These emulsions showed non- Newtonian behaviour. These investigators have proposed a correlation that fitted their experimental data with an absolute error of 5%.

2.4.6 Emulsion swelling

Swelling refers to the phenomenon of increase of volume of the emulsion during operation due to incorporation of the external phase solvent or the external phase itself into the emulsion globules.

Swelling is detrimental to the ELM extraction process on account of the following: -

- Swelling dilutes the solute that has been concentrated in the internal phase of the emulsion. It also dilutes the reactive agent present in the inner phase thereby lowering the effectiveness of the extraction/ stripping.
- Swelling changes the rheological properties of the emulsion and hence its dispersion characteristics. It causes difficulty in emulsion transport and phase separation. (Martin and Davies 1977, Draxler and Marr 1986, Xuan – Cai and Fu-quan 1991)
- Swelling makes the membrane thinner leading to less stable emulsions. (Matsumoto *et al.* 1980, Magdassi and Garti 1984, Ma and Shi 1987)

There are two mechanisms of emulsion swelling (i) Osmotic swelling (ii) Swelling due to entrainment of the external aqueous phase. Osmotic swelling is driven by differences in osmotic pressure between external and internal phases.

Fig. 2.7 illustrates the effects of osmotic swelling eventually leading to drop rupture. Osmotic swelling itself could take place by two different mechanisms in W/O emulsions.

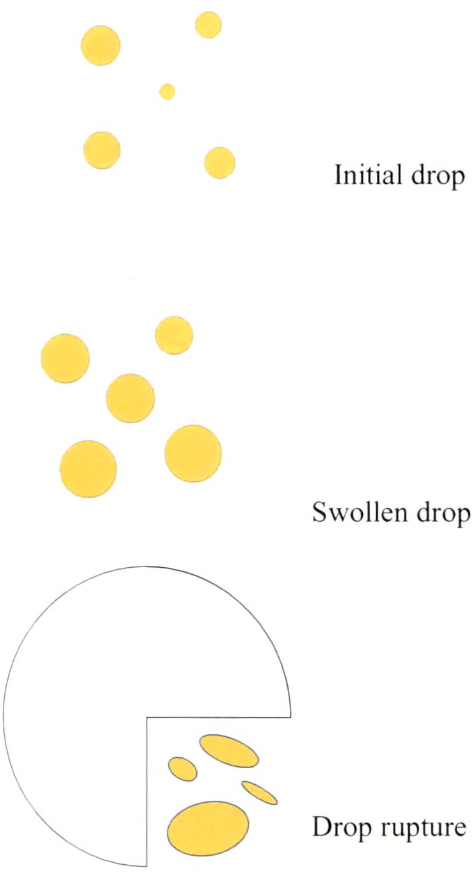


Fig. 2.7 Osmotic pressure effects leading to swelling and rupture of W/O emulsion droplets

Based on experiments with non-dispersed W/O emulsions contacted with water in a two compartment cell, Colinart *et al.* (1984) postulated that there was a complex formation between water and surfactant molecules. The hydrated surfactant then diffuses across the membrane interface between the membrane and internal water droplet phase that has low water activity and gets dehydrated.

The other osmotic swelling mechanism proposes the transport of water by reverse micelles. The micelle forms at the interface next to external aqueous phase with high water activity and is dehydrated at interface next to internal droplet phase with low activity. Skelland and Meng (1996) suggested that solvation of transferring solute by the external solvent was also a cause for emulsion swelling.

Matsumoto *et al.* (1980) observed a trend of decreasing water permeation coefficient with increasing oil soluble surfactant concentration from 10 to 50 % w/w. This behaviour was attributed to the increase of viscosity of the membrane phase caused by high surfactant concentration. Garti *et al.* (1987) reported that permeation coefficient increased with an increase in oil soluble surfactant concentration in the membrane phase in the range of 2 – 20% w/w and approached an asymptotic value. Jager-Lezer *et al.* (1997) verified that oil soluble surfactant was a major factor for water migration in multiple emulsions, with water transport rates increasing with increasing oil soluble surfactant concentration. Further their work showed that water-soluble surfactant present in the water phase had no effect on the water transport into W/O emulsions.

Swelling mechanism via entrainment of the external phase into the emulsion accounts for the swelling due to repeated coalescence and redispersion of the emulsion globule as reported by Ma and Shi (1987). Evidence supporting this idea was the increase of swelling observed with increasing stirring speed by Yan *et al.* (1987) and Ding and Xie (1991). Some investigators like Itoh *et al.* (1990) believe that swelling occurred due to secondary emulsification of the entrained solvent due to excess surfactant in the primary emulsification while others like Ohtake *et al.* (1987) contented that mode of mixing during dispersion operations had an important influence on the swelling behaviour.

Yan and Pal (2001, 2003) reported that swelling rates initially increased, reached a maximum and then fell off with an increase in surfactant concentration. Further, they also reported a reduction in the permeation coefficient with an increase in the internal phase fraction of the emulsion. Wan and Zhang (2002) in a comprehensive study on swelling characteristics of W/O/W emulsion liquid membranes reported that osmotic swelling might cause an increase or decrease in volume of the internal phase depending on whether internal phase or external phase has higher ionic strength.

Numerous studies on ELMs have shown that practically all surfactants and extractants will carry water within the W/O emulsion to some extent. Thus swelling is inevitable but swelling can be suppressed by a variety of methods as listed below:

- Using suitable surfactants to minimize surfactant hydration and micelle formation for example glutamic acid ester surfactants cause negligible swelling as reported by Goto *et al.* (1987) and Nakashio *et al.* (1988).
- Increasing membrane viscosity to increase membrane strength and resistance against water permeation.(Terry, Li and Ho 1982 and Colinart *et al.* 1984)
- Increase membrane thickness by increasing volume ratio of the membrane internal phase thus the resistance to water permeation as reported by Ma and Shi (1987).
- Addition of non transportable salts to the external phase to match the water activity of the external and internal phase Lobrach *et al.* (1986)

- Addition of an additive to obtain preferential micellization of the surfactant with the additive rather than with water. Gadekar, Mukkolath and Tiwari (1992) added cyclohexane to the membrane phase containing Span 80 and could contain swelling to a considerable extent.

2.4.7 *Membrane Leakage*

Membrane leakage refers to the undesired release of the inner droplet phase contents of an emulsion into the bulk of continuous phase. Leakage occurs by two mechanisms

- Diffusion of inner droplet phase components through the membrane.
- Emulsion globule rupture during dispersion, which leads to dumping of the encapsulated inner phase components of the emulsion into the external bulk phase as shown in Fig. 2.8.

Most investigators attributed the second mechanism to be the main cause of membrane leakage.

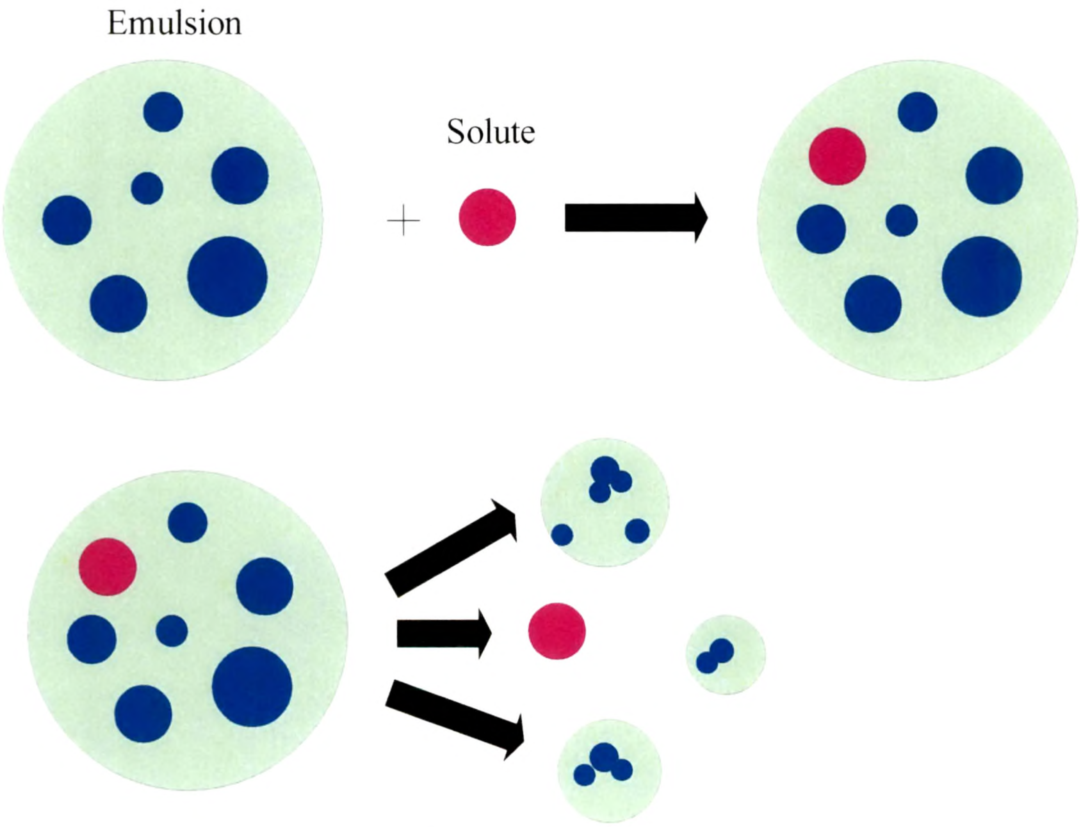


Fig. 2.8: Schematic diagram of solute permeation and emulsion breakage

Leakage is more detrimental to ELM extraction process in comparison with swelling. Leakage causes a decrease in driving force of mass transfer lowering the mass transfer efficiency. Membrane leakage is often attributed to poor membrane stability. Membrane stability in turn is influenced by numerous factors such as membrane formulation, emulsion preparation technique, pH of feed, pH of internal phase, internal phase reagent concentration, surfactant concentration in the membrane phase also the carrier concentration in the membrane phase.

Ho and Li (1992) reported that initial leakage of internal phase after emulsion addition to feed could be attributed to the lack of ideal encapsulation of the internal phase in the membrane matrix. Investigations by Abou-Nemeh and Van Peteghem (1992) revealed that the emulsion leakage passed through a minimum for a certain composition of the membrane.

Some investigators have attempted to quantify the extent of membrane leakage by globule rupture mechanism using tracer techniques. The tracer added to the inner droplet phase has to be chosen with care, it should have negligible solubility in the membrane phase thereby ensuring that its presence in the external phase could only be attributed to globule rupture and no other transport mechanism.

Takahashi *et al.* (1981) used a wide range of tracers such as NaSCN, $CuSO_4$ etc. to determine the extent of leakage under acidic and alkaline conditions in the inner droplet phases. They observed that under alkaline conditions the emulsion leakage was more severe. They concluded that stability of W/O/W emulsions depended on ionic species and its concentration in the inner aqueous phase.

Teramoto *et al.* (1983), Abou-Nemeh *et al.* (1992) used lithium as tracer to quantify globule rupture. Kulkarni *et al.* (2001) used nickel salts as tracers in presence of acids such as H_2SO_4, HCl, HNO_3 and methane sulfonic acid they observed that leakage is closely related to swelling of the emulsion they showed that conditions producing minimum swelling led to minimum globule rupture. Further Kulkarni *et al.* (2002) also used lithium tracer to quantify emulsion leakage during uranium extraction into emulsion liquid membranes. They report 50% emulsion swelling in a time span of 25 minutes and in the same time span about 20% emulsion leakage.

2.4.8 Demulsification

Emulsions are constructs and breaking of emulsion is to disrupt the structure of the system to fall apart into its component phases. Demulsification of loaded emulsion in order to recover the concentrated solute and recycle of membrane phase is therefore a key step influencing the commercial success of liquid membrane process.

Emulsion breaking involves two processes sedimentation and coalescence. There are two principal approaches for demulsification 1) Chemical treatment 2) Physical treatment.

Chemical Treatment: This method involves the addition of a demulsifier to the emulsion, it is known to be an effective method but necessitates an additional purification stage to purify the membrane material. The role of the demulsifier is to shift the equilibrium of the system to separate oil and water phases. Since the emulsions used in ELM processes are stabilized by surfactants, the role of the additive is to counteract the effect of the surfactant. Three approaches are possible (Lissant 1986, Morrison and Ross 2002): -

> **Chemical Reaction**: Chemical reaction between the surfactant and additive modifies the surfactant making it unsuitable for the particular system. One of the simplest of these cases is the neutralization of the ionic surfactant, this leads to change in the interfacial film and the emulsion may break. The surfactant has to be dealt with mole for mole as per stoichiometric requirement. This approach is sometimes expensive.
>
> **Solubility:** Increasing the solubility of the surfactant in one of the bulk phases is a common way of breaking emulsions, for example addition of an alcohol or ketone to the system may increase the solubility of the surfactant in one of the phase and thereby pull it from the interface resulting in emulsion splitting. Gadekar (1992) used acetone to demulsify W/O emulsions loaded with nitrophenol's, El Sayed (2003) used n-octanol in volumetric ratios of 1:10

with ELM to break uranium loaded emulsions. Okamoto *et al.* (2000) used 2-ethylhexanol to break W/O emulsions loaded with mixed heavy metals.

Structural Changes: Many commercial demulsifiers work by disruption of the oriented structure of the surfactant. Often these materials are effective in extremely small amounts, they do not operate on mole to mole basis. Most of these materials are not very soluble in either of the phases. This helps them concentrate at the interface even when small amounts are added, resulting in a high local concentration of the additive at the interface. Since emulsions are constructs the interfacial phases owe its effectiveness to its oriented structure. The forces that hold the interfacial phase in a particular pattern are short-range forces. If some other material can insert itself between the surfactant molecules, it increases the intermolecular distances and weakens the binding force of the structure that results in emulsion splitting.

Physical Demulsification: Physical methods include heating, centrifugation, ultrasonic, high shear and high voltage electrostatic fields. The most wide spread and effective methods of demulsification are heating and the use of high voltage electrostatic fields.

Demulsification by heating: Elevation of temperature leads to an increase in solubility of the surfactant in both oil and water phases thereby weakening the interfacial film that binds the oil to water (Lissant 1986). Since oil phase has a larger coefficient of expansion than water, the decrease in oil density with enhancement of temperature is more pronounced than the decrease of density of water and these two phenomena combined with reduction of viscosity of both phases promote the segregation and separation of the oil and water phases of the emulsion.

Heat treatment on its own shows slow demulsification kinetics hence it is often used in conjunction with some other technique, which improves the coalescence kinetics (Larson *et al.* 1994). Heating method has been used mostly for laboratory scale operations using ELM (Kulkarni *et al.* 2001, 2002). It must however be noted that heating can lead to degradation of membrane phase as well as the surfactant.

Demulsification using electrostatic field: Electrostatic coalescence is a technique widely used to separate dispersed aqueous droplets from non-conducting oils. Use of high voltage electrostatic field is the most efficient and economic way for breaking W/O emulsions. The field polarizes and elongates water droplets and can cause unidirectional migration of the droplets by electrophoresis or dielectrophoresis mechanism. It is extensively practiced in the petroleum industry to separate brine emulsified in crude oil. However, the conventional electrostatic coalescer for crude oil dewatering cannot be directly used for breaking W/O emulsions in ELM processes.

This is primarily because W/O emulsions prepared for ELM processes are made intentionally and therefore contain high concentration of potential emulsifying surfactants further the properties of the oil phase must be preserved for remulsification. Secondly the water content in emulsions used for ELM process is expected to contain much more water (almost 10 times more) than the water content of crude oil emulsions.

The emulsion breaking process occurs in three stages: drop coalescence and growth, droplet settling and coalescence of large water and oil droplets in their respective continuous phases in the coalescer. The coalescer throughput can be limited by any of these three stages.

Pearce (1954) microscopically studied the effect of an applied electric field to a 10% W/O emulsion. He observed that water molecules form chain of droplets oriented along the direction of electric field. The chain formation and elongation of water droplets disturb the thin film between the droplet surfaces and lead to coalescence. Since the attractive force between the water droplets is proportional to the square of applied field, high voltages are used in electrostatic coalescers.

However, the maximum voltage is limited by sparking, which occurs when the water chain formed extends from one electrode to another in non-insulated coalescers. Lowering the voltage results in slow coalescence kinetics as well as formation of stable sponge emulsion, a high water content (internal phase fraction about 90%) W/O emulsion. This indicates an ineffective coalescence of large water droplets with bulk water phase in an electrostatic coalescer. To minimize the formation of sponge emulsion the voltage must exceed certain critical value. Brown and Hanson (1968) have observed that the critical field strength to be the same for a DC or AC field up to 10,000 Hz.

The main factors affecting demulsification are the emulsion drop sizes, applied voltage, frequency and waveform. Smaller emulsion drop sizes lead to low rates of coalescence.

Hsu and Li (1985) made a detailed study on electrostatic coalescence of liquid membrane emulsions. They observed that increasing the voltage from 13 kV to 20 kV increased the coalescence rates. However, excessively high voltages could cause sparking and should be avoided. They also found that an optimal gap size existed at which sponge emulsion accumulation was minimum. Draxler *et al.* (1988) observed that voltage could be reduced when frequency was enhanced for the same degree of demulsification.

Feng, Wang and Zhang (1988) also noted that coalescence efficiency increased when frequency increased. They observed that under 5 kV for 10 min the coalescence efficiency increased from 50 to 100% when frequency increased from 0.6 to 5 kHz. Further they observed that stirring the emulsion during the demulsification process could accelerate the coalescence rate. They reported a 5 to 6 fold increase in rates as stirring speeds increased from 0 to 200 rpm.

Draxler *et al.* (1988), Yan *et al.* (1987) investigated the influence of wave shape of alternating current on rates of coalescence and found that square wave form was much better than a triangle or sinus form. Draxler and Marr (1986) developed an electrostatic coalescer with two planar insulated electrodes in parallel. Insulated electrodes prevented sparking at high voltage, preclude electrolysis, protects electrode from chemical corrosion by an acid or base. This design was used for demulsification of zinc loaded emulsion membranes from wastewater in viscose fiber industry.

The effect of insulation on functioning of continuous coalescers was also studied by Hsu and Li (1985). They found that electrodes insulated by solid dielectric medium having dielectric constant of about 4 and a hydrophobic surface can break W/O emulsions at a faster rate with excellent quality of recovered oil for suitable re-emulsification. These investigators suggested that elevated temperatures might be necessary to accelerate coalescence for emulsions prepared with membrane phase having oil viscosity greater than 10 cp.

Membrane recycling and regeneration has not been systematically studied. Abou-Nemeh *et al.* (1992) found that recycling the membrane through the emulsification splitting loop gradually deteriorated the membrane after each cycle. The same investigators (Abou-Nemeh *et al.* 1993) also observed that the splitting efficiency of the emulsion was found to be proportional to the number of cycles used. The higher the number of cycles the easier the emulsion breakdown.

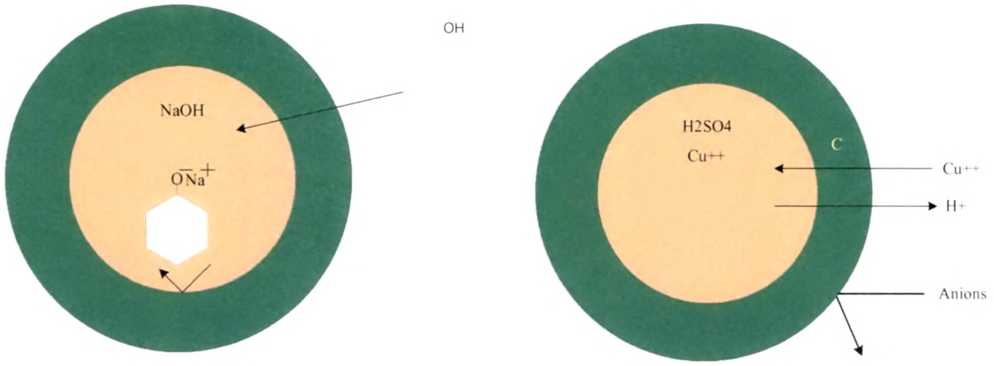
2.5 TYPE I FACILITATED TRANSPORT

The most effective use of ELM process is achieved when the flux through the membrane phase and the capacity of the diffusing species in the membrane phase are maximized. Maximization of the flux through the membrane phase can be achieved by maximizing the concentration of the diffusing species across the membrane.

There are two types of facilitation mechanisms to maximize the flux and capacity. Type I facilitation uses a reactive agent in the internal phase of the emulsion to irreversibly react with the solute and form a product that is incapable of diffusing back through the membrane, thus maintaining the solute concentration effectively at zero in that phase and thereby enhancing the mass transfer rates also encapsulating the product. Since diffusing solutes are soluble in the membrane phase the selectivity of solute separation depends solely on the partition coefficient of the solute.

Typical example of Type I facilitation are extraction of weak acids (phenolics, acetic acid etc.) from water streams. These solutes are soluble in the membrane phase and they diffuse through the membrane in their undissociated form and get neutralized in the internal membrane phase by a strong base present there. Since neither the strong base nor the resultant ionized salt is oil soluble they remain encapsulated inside the emulsion drops and thus get separated from the bulk continuous phase. Similarly weak bases (ammonia, aniline, amines etc.) could be removed from water streams using emulsion liquid membranes containing a strong acid.

In the other mechanism, Type II facilitation, the solute on its own is not able to diffuse through the membrane due to its negligible solubility in the membrane phase hence a transport facilitator or carrier is incorporated in the membrane phase to enhance the rates of transport. The carrier not only facilitates mass transfer but also enhances the separation selectivity. Fig. 2.9 illustrates the two facilitation mechanisms. Type II facilitation or carrier mediated transport is discussed in detail in section 2.6.



TYPE 1 FACILITATION

TYPE 2 FACILITATION
(CARRIER FACILITATED TRANSPORT)

Fig. 2.9: Schematic of the two Facilitated Transport Mechanisms

2.5.1 Extraction of Phenol

Li and Shrier {1972} first separated phenol from water using ELMs and it was the first application of removal of solute from aqueous streams. It is also the most extensively studied organic solute extracted by ELMs. More than a dozen experimental studies were reported in literature for phenol extraction from water streams. Mostly investigations were carried out in batch systems however; a few investigations were reported for continuous extraction of phenol.

To extract phenols from aqueous streams W/O emulsions containing NaOH in its internal phase are dispersed in the aqueous stream. Phenol diffuses across the membrane phase into the inner phase containing NaOH where it reacts to form sodium phenolate. The pH value of the external aqueous phase must be below 9 to keep the phenol in undissociated form, since phenol is soluble in the organic membrane only when it is undissociated. The dissociated form of phenol, phenolate, is not soluble in the membrane phase hence it remains in the inner phase as shown in Fig. 2.10

A comparison of the operating conditions and experimental parameters for phenol extraction into ELMs as studied by various investigators are listed in Table 2.2. The main variables studied are effect of stirring speed, internal reactive phase concentration; treat ratio (Volume ratio of emulsion to feed phase) and initial phenol concentration. Agitators used for stirring were mostly turbine type; some investigators also used marine propellers.

The surfactant (emulsifier) used in most investigations was the nonionic surfactant Span 80® or polyamine surfactant like ECA 4360®. Wide range of membrane materials has been studied from purely aromatic (Toluene) to purely aliphatic S 100N®. Initial phenol concentrations studied range from 100 to 5000 mg/L. Treat ratios studied range from 1:2 to1:20. NaOH concentration studied range from 0.1% to 20 % (wt) and the extent of phenol recovery range from 60% to 99%.

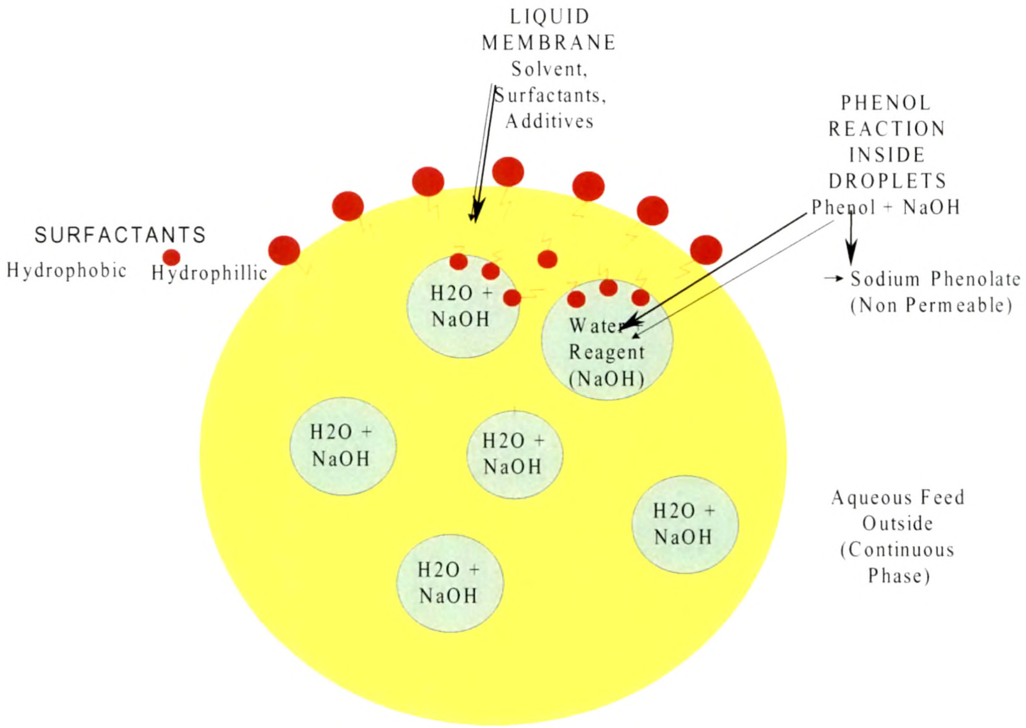


Fig. 2.10: Schematic of liquid membrane system for phenol removal

Chang and Li (1983) studied extraction of phenol into ELMs in a continuous counter-current extraction column 1.2 m long and 0.06 m in diameter. They contacted water having initial phenol concentration 500 mg/L with emulsion containing 0.5 M NaOH in the internal phase, the water flow rate was varied in the range of 82 to 150 ml/min and emulsion flow rates in the range 30 to 70 ml/min. Almost 98 % recovery has been recorded in most cases. The HTU of their column was about 160 to 190 cm. Kinugasa *et al.* (1995) studied phenol removal from dilute solutions in counter-flow spray columns.

Kataoka *et al.* (1997) studied phenol extraction in stirred counter-current columns. They studied the effect of diluents, surfactants and internal aqueous phase composition of the emulsion on the extent of extraction. They observed that emulsions made with Span 80 containing NaOH solution in the internal phase removes phenol effectively but the emulsion could not be demulsified on the other hand when Na_2CO_3 was used in the internal phase the resulting emulsion could be easily demulsified however the phenol extraction reduced drastically. These investigators suggested use of mixed NaOH/ Na_2CO_3 solutions.

In case of phenols other weak acids if they happen to be present would compete with phenol in permeating through the membrane and react with the encapsulated caustic. Thus acetic acid, H_2S, HCN all of which have small dissociation constants and good solubility in the organic membrane layer will permeate along with phenol and accumulate in the inner phase. However strong mineral acids on account of their high degree of dissociation and low solubility in the oil phase will not tend to diffuse across the oil membrane. The net result is that Cl^-, SO_4^{2-}, etc are effectively excluded from the encapsulated caustic. Thus this method can be used to remove phenol even in the presence of large amounts of chloride.

The presence of bases such, as NH_3 and amines in the feed do not interfere with the removal of phenol. These materials are quite soluble in the oil film they will diffuse across the membrane but since they do not react with NaOH they will rapidly build up to about the same concentration inside and outside the liquid membrane and further permeation would come to a halt.

2.5.2 Extraction of phenol derivatives and other weak acids

Gadekar *et al.* (1992) studied the extraction of p-nitrophenols into ELMs. They studied the effects of agitation speed, surfactant concentration; treat ratio and internal phase fraction on the rates of extraction. As expected increasing stirring speeds led to greater globule rupture, rates of extraction decreased with increasing surfactant concentration and also with increasing treat ratios. Increase in the internal phase fraction increased the rates of extraction. These investigators also studied the extraction of o-nitrophenol and 2,4- di nitrophenol into ELMs, they observed that the rate of extraction of o-nitrophenol was higher than the other two solutes on account of higher solubility of o-nitrophenol in the oil phase. Luan *et al.* (2004) studied the extraction of nitrophenol compounds by ELMs. The initial concentration of nitrophenols was 1050 mg/L, treat ratio of 1:3, $\phi = 0.333$, NaOH concentration 2%, the total removal obtained was greater than 99%.

Borwankar *et al.* (1998) studied the extraction of 2-chlorophenols into ELMs, they primarily focused on the effect of internal phase leakage on ELM separations. These investigators reported only the effect of surfactant concentration on extraction rates and as expected increasing surfactant concentration leads to lower extraction rates, this aspect was well predicted by models developed in this work. Lin and coworkers (1993) studied the extraction efficiencies of 2-chlorophenols from aqueous solutions into ELMs under various operating conditions. They advocated use of multistage process in lieu of single stage operation for efficiency enhancement.

Table 2.2: Comparative overview of phenol extraction into emulsion liquid membranes as studied by different investigators.

S.No.	Investigators	Membrane Material	Surfactant	Stripping agent concentration	φ	Initial phenol Concentration ppm	Treat ratio	Stirring speed rpm	Temp. °C
1	Li & Shrier (1972)	S 100N	Span 80	NaOH (0.1-1 %wt)	-	1740,1000 and 200.	-	100 - 300	25
2	Chan & Li (1974)	S 100N	Span 80	NaOH (0.1-20 %wt)	0.465	1060	1:1.88	100-200	25
3	Matulevicius & Li (1975)	S 100N	Span 80 + ENJ 3029	NaOH (0.5 % wt)		1060	1 : 5	250,350,530	-
4	Terry, Li & Ho (1982)	S 100N+LOPS LOPS	ECA 4360 PIBSA poly	NaOH (10%wt) NaOH (10% wt)	0.465 0.444	5000	1 : 2.5 to 1 : 5	420 - 520	-
5	Ho, Hatton, Lightfoot & Li (1982)	S 100N	Span 80 ENJ 3029	NaOH (1.5 % wt)	0.363	770	1 :15	400 - 600	23
6	Chang & Li (1983)	Kerosene	Span 80	NaOH (1 % & 2% wt)	0.42-0.55	300-950	1:1.5, 1:2, 1:2.5, 1:3	200 - 350	20
7	Teramoto & Takihana (1983)	Kerosene	Span 80	NaOH (0.1 to 0.3 M)	0.5	500 - 2000	1 : 6.5	188	25
8	Kim, Choi & Ihm (1983)	Mineral oil	Span 80	NaOH (0.25 – 1% wt)	0.5	1000 and 3000	1: 3 1 : 4	200	20
9	Boyadzhiev, Bezenshek & Lazarova (1984)	n-paraffin	Span 80	NaOH (0.5 % wt)	0.5	120	1 : 20 1 : 10	120 (impeller dia. 60mm) 50,60 (impeller dia. 160 mm)	25

Table 2.2…..Continued

S.No.	Investigators	Membrane Material	Surfactant	Stripping agent concentration	φ	Initial phenol Concentration ppm	Treat ratio	Stirring speed rpm	Temp. °C
10	Fudu, Xinpei & Zhang Youanqi (1985)	Liquid paraffin	Polyamine	NaOH (0.1M, 0.25 M 0.5 M, 2M)	0.5	130 to 480	1 : 10	--	20
11	Kataoka, Nishiki & Kimura (1989)	Kerosene + Liquid paraffin	ECA 4360 J Span 80	NaOH (0.1 M)	0.2, 0.333 & 0.5	940	1 : 6.5	150, 198, 300 & 402	25
12	Kakoi et al. (1996)	Shellsol 71	Span 80 PX 100 Glutamic acid esters	NaOH (0.05 to 0.2 M)	0.5	50 - 600	1 : 5	300	30
13	Solanki & Sengupta (2003)	Toluene	Span 80	NaOH (0.2 – 0.35M)	0.45	100 - 500	1 : 10 1 : 20	135 - 180	30

Correia and de Carvalho (2000) also studied the extraction of 2-chlorophenol into ELMs. They reported the effect of several variables such as membrane composition, internal reagent concentration, solute concentration, stirring speed, treat ratio and internal phase fraction on the rate of extraction. They found only the last three variables showed significant effect. This behaviour could be attributed to the high distribution ratio of 2-chlorophenol between the external and membrane phases

An interesting study on the extraction of weak acids into ELMs was reported by Ma and Shi (1987). They investigated the extraction of acetic acid into ELMs using kerosene membranes containing N205 non-ionic polyamine surfactant. They studied the variation of stirring speed, treat ratio and ratio of reagents on the rates of extraction. Acetic acid as a weak acid has a low but significant solubility in kerosene. Therefore, it can permeate through the kerosene membrane making it an appropriate candidate for Type I facilitated transport. However, in their experiments Ma and Shi used emulsions formulated with N 205 surfactant; N 205 can react with acetic acid due to its three –N-- functional groups. Therefore N 205 also acted as a carrier for acetic acid in this system. The net result was that acetic acid was transported into the ELM by Type I as well as Type II facilitated transport mechanisms.

2.5.3 Extraction of weak bases

The potential of ELMs for removal of ammonia in the tertiary treatment of wastewaters was recognized by a number of investigators (Li and Shrier 1972, Maugh 1976, Frankenfeld and Li 1977, Halwachs and Schugerl 1978). The mechanism of removal of ammonia is just the same as that of phenol with the only difference being that ammonia is an alkaline substance therefore requiring an acidic stripping phase. Further the pH of wastewater must be above 10 in order to convert ammonium ion to free ammonia that is soluble in the oil membrane phase.

Lee and Chan (1990a, 1990b) carried out comprehensive investigations on ammonia extraction into ELMs using H_2SO_4 as the reactive agent in the internal emulsion phase. Paraffin oil was used as the membrane phase. Two surfactants Span 80 and ECA 4360 were tried out. The authors claimed Span 80 to be a better and more active emulsifier. Further these investigators observed that varying the volume fraction of the internal phase ϕ from 0.25 to 0.5, the rates of extraction were maximized at ϕ = 0.4.

Teramoto *et al.* (1981) studied extraction of amines (aniline, m toludine and p toludine) into W/O emulsions made from kerosene containing Span 80 with HCl as the internal phase. These investigators developed a mass transfer model that accounted for the diffusion both in and around a W/O emulsion drop.

2.5.4. Biomedical applications of emulsion liquid membranes.

ELMs are known to have potential for biomedical applications such as artificial kidney. Asher (1980) studied recovery of urea using S100N membrane containing Span 80 as emulsifier. Volkel *et al.* (1982) studied the extraction of free phenol from blood by a liquid membrane enzyme reactor. O'Brien and Senske (1989) investigated recovery of acrylic and propionic acids from fermentation broths using S100N membranes with Paranox 100 as the emulsifier. Stoica-Guzun *et al.* (1996) studied encapsulation of urea into ELMs prepared from a variety of membrane materials such as paraffin oil, sunflower oil and n-hexane using egg Lecithin as emulsifier and glycerol as stabilizer. The membrane was so formulated that it could be used in human body for treatment of chronic uremia. This is an example of solute transport when no facilitation is present.

2.5.5. Commercial applications of Type I transport.

Removal of phenol from wastewaters was commercialized in 1986 at the Nanchung Plastic factory in Guangzhaou, China. The surfactant used in the ELM systems was LMS-2 an anionic type surfactant with average molecular weight of 5000 and viscosity of 8000 to 10000 cp and specific gravity 0.83 to 0.86 (at 25°C). Kerosene was used as the membrane phase and stripping phase NaOH concentration was 1.25 M. Initial feed concentration was 1000mg/L and almost 99% phenol removal was achieved.

2.6 TYPE II FACILITATED TRANSPORT

Type II facilitation is usually associated with solutes that are insoluble or sparingly soluble in the membrane phase. The main area of application of this mechanism is in the extraction of metal cations and anions from aqueous solutions. Since such extractions are energetically very unfavorable, it is necessary to neutralize the ionic charge prior to extraction. In ELMs, this is attained by direct reaction between the ionic species of interest and an appropriate organic compound present in the membrane phase to form a neutral species soluble in the organic membrane phase. Such reagents that are used for transport facilitation are called carriers or extractants.

The carrier-solute reaction is essentially an equilibrium (reversible) chemical reaction. Further, association with the extractant generates an extractant-ion complex that is highly soluble in the organic membrane phase. Thus the extractant shuttles the metal ion within the emulsion membrane globule. The internal phase of the emulsion is designed to carry out the stripping reaction at the membrane- internal phase interface using an appropriate stripping agent. The metal ion is released in the internal phase rendering the extractant free to shuttle more metal ions into the internal membrane phase. This process continues so long as the internal stripping phase is not totally exhausted.

The carrier is the most important ELM component in type II facilitated transport. The role of the carrier is not only to facilitate the mass transfer but also to enhance the separation selectivity. Such transport activity, called the carrier-mediated transport, is appropriately illustrated with an example of copper transport from wastewaters into emulsion liquid membranes as shown in Figure 2.11.

The bivalent copper ion reacts with a liquid ion exchange reagent 'RH' present in the membrane phase as a carrier at the external surface of the emulsion globule according to the following reaction (where underline indicates the species in organic phase)

$$\underline{2RH} + Cu^{2+} \rightleftharpoons \underline{R_2Cu} + 2H^+$$

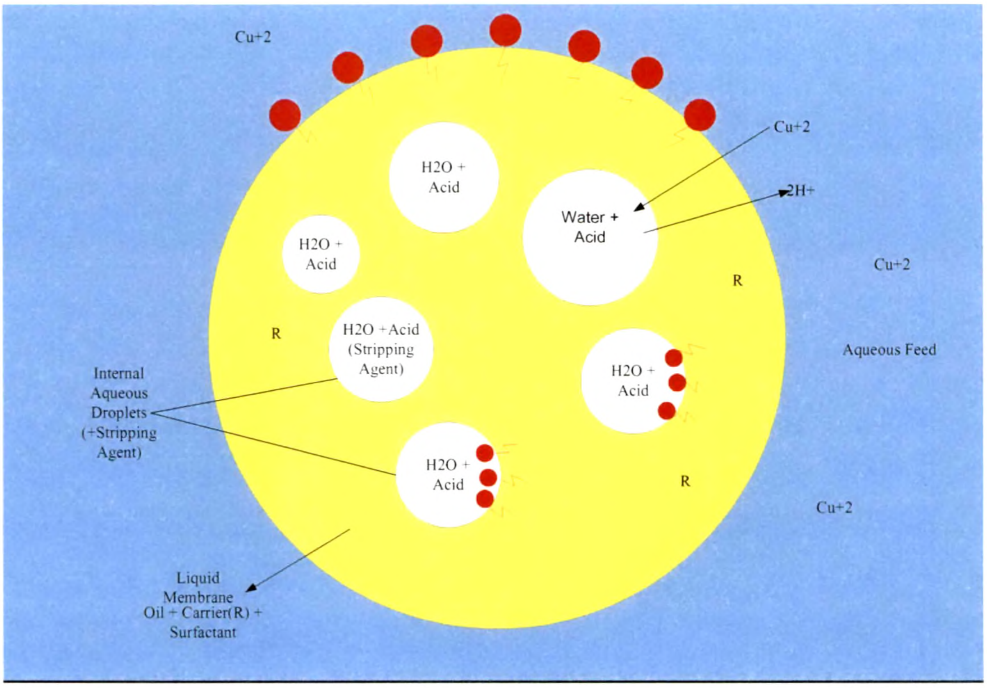


Fig. 2.11: Copper transfer in emulsion liquid membrane globule

The complex R_2Cu diffuses through the membrane phase to the inner aqueous phase where the Cu ion gets stripped from the carrier using an acid as per the following chemical reaction:

$$2H^+ \quad + \quad \underline{R_2\,Cu} \quad \rightleftharpoons \quad Cu^{2+} \quad + \quad \underline{2RH}$$

The liberated carrier is free to shuttle back to the bulk phase – membrane phase interface to scavenge more Cu^{2+} ions while the stripped copper ion is effectively encapsulated in the internal phase of the membrane.

With reference to metals the extractable species can be divided into four categories: -

- Metal cations such as Cu^{2+}, Ni^{2+} etc.
- Complex metal cations such as MoO_2^{2+}
- Complex metal anions, for example $UO_2(SO_4\}_3^{4-}$ and
- Neutral metal salts like $UO_2(NO_3)_2$

Consequently the carriers can also be classified according to functional groups into three classes:

- Acidic
- Basic
- Neutral

2.6.1 *Acidic Carriers:*

Acidic carriers or extractants are further characterized by structure, extraction mechanism, and the metal species extracted into two different classes: -

- Chelating carriers
- Organic acids

2.6.1.1 Chelating carriers:

Chelation refers to 'claw', which is a graphic description of the way in which the organic carrier binds the metal ion. The carrier chemically bonds the metal in two places in a manner similar to holding an object between the thumb and the index finger (Redbook 2001). Upon bonding with the metal ion the extractant releases a hydrogen ion into the aqueous solution from which the metal is extracted. Chelating carriers must contain at least two donor groups, one with a dissociative proton (monobasic acids) such as carboxyl group, oxime group, hydroxyl group, imino group etc to bind the metal ion, the other donor group containing non- dissociative protons, such as carbonyl group, nitroso group, amino group, trivalent nitrogen atom, is arranged to form the chelating ring with metal ion.

Chelating carriers have the following characteristics:

- The solubility of commercial carriers with a long alkyl chain is low in the aqueous phase to prevent carrier losses.
- The acidity of chelating carriers is weak, the pKa in the aqueous phase being large ranging from 6 to 12.5.
- Chelating carriers have high selectivity for metal ions that can be further modified by changing the pH of the aqueous phase.
- The rates of metal extraction with chelating carriers are slower than in the extractions with basic or neutral carriers such as trioctyl amine and tri butyl phosphate.

Harada & Miyake (1989) have presented an excellent review concerning the extraction equilibria, interfacial properties of chelating reagents (carriers) and kinetics of metal extraction by such chelating carriers.

Chelating reagents are extensively used for hydrometallurgical extraction processes and are commonly called as metal extractants. General Mills Chemical Company Inc. introduced the LIX series of hydroxime extractants in 1960's (these products are now produced and marketed by Cognis Inc.). LIX reagents are widely used in copper separation processes.

Currently the most widely used members of this family are the following:

- LIX ®84 / Ketoxime: Predominantly 2-hydroxy-5-nonylacetophenone oxime in mixture with a small amount of 5-dodecyl salicylaldoxime in a high flash point diluent. It is an excellent copper extractant of moderate strength that gives good physical performance under a wide variety of conditions but most useful above pH of 1.6 to 1.8.
- LIX ® 860/ Aldoxime: Predominantly 5-dodecyl salicylaldoxime with a small amount of 2-hydroxy-5-nonylacetophenone oxime. LIX 860 is very strong copper extractant even at pH values less than 1.0. This reagent is often used in blended with ketoximes so that the chelated copper is effectively stripped.
- LIX ®984: An equivolume mixture of LIX 84 and LIX 860 it reflects the most desirable characteristics of the components, the fast kinetics of salicylaldoximes with proven stability and excellent physical performance of the ketoximes. These mixtures were introduced in 1982 and are currently the most widely used copper extractants in the world.

Other notable β hydroxime reagents used commercially are SME 529 (Shell now Henkel), P17 and P50 (Acorga). β hydroxy quinolines such as Kelex 100 (Ashland Chemical Co.) are alternative Copper extractants. β diketones such as acetylacetone, benzoylacetone are also chelating extractants and were once used for copper extraction from ammonical solutions but are now phased out after introduction of LIX 84 family of extractants.

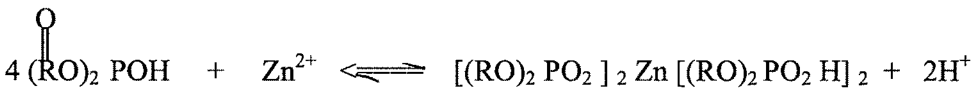
2.6.1.2 Organic acid carriers:

Reagents that belong to this class include carboxylic acids, organosulfonic acids and the organo -phosphoric acids, - phosphonic acids, - phosphinic acids with their mono and di thio derivatives.

Carboxylic acids are relatively weak extractants and are fairly soluble in the aqueous phase at acidities where significant extraction occurs. Napthenic acid has been used as carrier for Ni^{2+} and Co^{2+} separations. Commercially carboxylic reagents Versatic 10 (Shell) also Versatic 911 have been used for extraction of zinc and cadmium.

Sulfonic acids are much stronger extractants. A major problem is their very high surface activity that can lead to difficulties in phase separation. Sulfonic acids tend to form micelles even at very low organic – phase concentrations. The presence of micelles dominates the whole extraction chemistry of Sulfonic acids. Commercially SYNEX 1051 (King Industries Inc.) an aryl sulfonic acid has been used for magnesium extraction.

The organo – phosphoric acid Di – 2- ethyl hexyl phosphoric acid (D2EHPA) is used for the extraction of uranium from leach liquors in the DAPEX process. It is also used for a number of other applications including zinc extraction, Co – Ni separation, rare earth separations etc. The chemistry of this type of extractant has some characteristics that resemble chelating extractants and some that are similar to solvating extractants this dual behaviour is illustrated by the following reaction:



$$4\,(\overset{O}{\overset{\|}{R}}O)_2\,POH \quad + \quad Zn^{2+} \rightleftharpoons [(RO)_2\,PO_2\,]_2\,Zn\,[(RO)_2PO_2\,H]_2 \;+\; 2H^+$$

Two D2EHPA molecules lose a proton like a chelating reagent while two other D2EHPA molecules solvate the zinc similar to solvating type extractants. The pH extraction characteristics of D2EHPA with respect to several metals are reported in literature (Sole and Cole 2002; Lo, Baird and Hanson 1983)

In commercial extractants the change from phosphoric acid structure (D2EHPA) to phosphonic acid structure (PC-88 of Daihachi) to phosphinic acid (Cytec's CYANEX 272) results in dramatic enhancement of selectivity for some metal cations. Sole and Cole (2002) reported that Co – Ni separation factors increase from 14 to 280 to 7000 when the order of extractants are changed from phosphoric to phosphonic to phosphinic acids.

Sulfur substituted organo phosphorus acid extractants became commercially available in the 1990's. The mono and dithio analogs of CYANEX 272 (CYANEX 302 and CYANEX 301, respectively) are stronger extractants because of the electron withdrawing effect of sulfur atoms. The extraction of base metal cations from higher acidity leach liquors is therefore possible. It is interesting to note that there is also a change in the relative order of extraction of the cations as shown below:

D2EHPA	Fe(III) > Zn > Ca > Mn > Cu > Mg > Co >> Ni
CYANEX 272	Fe(III) > Zn > Cu > Mn > Co > Mg > Ca > Ni
CYANEX 302	Cu > Fe(III) > Zn > Co > Mn > Ni>> > Mg
CYANEX 301	Cu > Zn > Fe(III) > Co > Ni >> Mn >>Mg

This provides some flexibility in reagent choice to achieve desired selectivity for particular extractions.

2.6.2 Basic Carriers

Basic carriers are essentially liquid anion exchangers; they are generally protonated forms of primary, secondary and tertiary high- molecular weight amines and quaternary compounds. The extraction of solute is by ion – pair formation whereby a large positively charged organic moiety causes the extraction of a large anionic metal complex into the organic phase with concomitant expulsion of a small common anion to the aqueous phase.

In aqueous solutions many metal ions can form a variety of anionic complexes with sulfate, halide, cyanate, thiocyanate and a number of other anionic ligands. Examples of anionic metal complexes that commonly exist in solutions in hydrometallurgical and electroplating processes are $Cd(CN)_4^{2-}$, $Cr_2O_7^{2-}$, MoO_4^{2-}, $UO_2(SO_4)_2^{2-}$, $V_3O_9^{3-}$ etc. The ease of formation of anionic complexes of different metal ions with the anion ligand in the aqueous solution varies greatly; for this reason, selective extraction is obtained by the use of suitable amines. For ELM metal extractions primary and secondary amines show poor emulsion stability and are usually not recommended (Draxler and Marr 1986). Thus tertiary amine such as trioctylamine (TOA), tri-n-octylamine (TNOA) and the commercially available Alamine® extractants are widely used in ELM studies. Similarly quaternary ammonium compounds such as Aliquat® 336 (tri-(C_8C_{10})methyl ammonium chloride) is widely used for solutions with high pH.

Quaternary ammonium compounds have been reviewed by Marcus and Kertes (1969). A feature of these compounds is their ionic character, which is retained under both acidic and basic conditions. They fall under two distinguishable groups according to their solubility, surface activity and tendency for molecular association. Those compounds with 24 or more carbon atoms per molecule are readily soluble in organic solvents and give a high distribution coefficient when distributed between an aqueous electrolyte and an immiscible organic phase. Quaternary ammonium compounds that contain five or less carbon atoms are readily water-soluble. High molecular weight salts are only sparingly soluble in water and behave as strong electrolyte.

In organic solution quaternary ammonium salts tend to aggregate, increasingly with increase in the molecular weight of the salt. Normally the high molecular-weight salts are readily soluble in non-polar aromatic hydrocarbons and the more polar solvents such as ethylene dichloride but show only sparing solubility in aliphatic hydrocarbons. Quaternary ammonium salts exchange anions by means of following reaction: -

$$\underline{\mathrm{R_4N^+A}} + \mathrm{B^-} \rightleftharpoons \mathrm{R4}\underline{\mathrm{N^+B^-}} + \mathrm{A^-}$$

(Where underline denotes species in organic phase)

In contrast primary, secondary and tertiary amines require protonation before they can act as anion exchangers and thus also have acid extracting properties in free – base form:

$$\underline{\mathrm{R_3N}} + \mathrm{H^+} + \mathrm{A^-} \rightleftharpoons \underline{\mathrm{R_3NH^+A^-}} + \mathrm{B^-} \rightleftharpoons \underline{\mathrm{R_3NH^+B^-}} + \mathrm{A^-}$$

Grinstead and Davis (1968) found that increasing substitution of the nitrogen by alkyl groups result in the increase in the base strength from primary to tertiary amines however, in solution the increasing stearic hindrance by the bulky alkyl groups impedes solvation of the cation – anion pair and thus reduces the stability of the salt relative to the free amine. Base strength increases with increasing concentration of the amine salt and thus is attributed to the aggregation of the salt in organic phase. The degree of aggregation depends on the diluent (membrane material) and the nature of the ammonium cation and anion. In toluene, alkyl ammonium chloride salts increase in degree of aggregation in the order: tertiary alkyl ammonium < secondary < primary.

Water uptake by the organic phase is proportional to the amine salt concentration and decreases with increasing anion size. The large amines do not seem to be hydrated very much in common diluents. The degree of hydration of the free base increases in the following order: tertiary < secondary < primary. The amount of water coextracted is related to the ability of the diluent to solvate the amine salt – ion pair. Roddy and Coleman (1969) studied extraction of water by tri-n-octyl amine and found that in benzene the amount of water extracted by amine salt always exceeded that extracted by the free base and increased in the following order: acetate < nitrate < chloride < sulfate. The effect of coextracted water on degree of extraction is not fully clear. However, from ELM extraction point of view water extraction would lead to excessive swelling and eventual rupture of emulsion globules.

Extraction of metal complexes can proceed by either an anion exchange reaction or addition reaction as follows:

$$\underline{R_4N^+X^-} + MY^-_{n+1} \rightleftharpoons \underline{R_4N^+MY^-_{n+1}} + X^- \qquad \text{(i)}$$

or

$$\underline{R_4N^+X^-} + MX_n \rightleftharpoons \underline{R_4N^+X^-_{n+1}} \qquad \text{(ii)}$$

Both extraction mechanisms take place even when the anion in the anion in the aqueous phase and the organic phase is the same. The controlling factor is the free concentration of X^- in the aqueous phase and the dominant species present in the aqueous phase ($MX^{(n-1)+}$, $MX_2^{(n-2)+}$,...., MX_n etc.); thus a knowledge of aqueous phase chemistry of these systems is of prime importance. The controlling factor is the free concentration of X^- in the aqueous phase. At high X^- concentration reaction (ii) will dominate whereas at low X^- concentrations reaction (i) will predominate.

The interaction of the amine salts and quaternary ammonium ions with metal anionic complex is mainly electrostatic; thus as degree of extraction is due to the extent of ion pair formation, selectivity will depend on charge, ion size, and extent of complex formation in the aqueous phase. Selectivity is generally achieved by varying the ligand concentration in the aqueous phase.

Transport of metal ions through liquid membranes containing tertiary amines follow two possible mechanisms depending on the stripping agent used:

Co-transport: If a basic solution is used as stripping agent in the internal aqueous phase; the permeation of the metal anion across the membrane is coupled to the transport of hydrogen ions in the same direction. Dichromate extraction by tertiary amines is a good example of this transport mechanism:

Extraction:

$$\underline{2R_3N} + 2H^+ + Cr_2O_7^{2-} \rightleftharpoons \underline{(R_3NH)_2Cr_2O_7}$$

Basic stripping:

$$\underline{(R_3NH)_2Cr_2O_7} + 4\,(Na^+ + OH^-) \rightleftharpoons \underline{2R_3N} + 2(2Na^+ + CrO_4^{2-}) + 3\,H_2O$$

where R_3N is the tertiary amine. Stripping with base regenerates the amine, which then re-extracts additional metal ions from external aqueous phase.

Counter-transport: If an acid serves as the stripping agent in the internal aqueous phase, the permeation of metal anion obeys the counter transport mechanism in which metal anions are transported in the direction opposite to the coupled anions. Dichromate extractions with quaternary ammonium salts obey the counter-transport mechanism in ELM systems

Extraction:

$$\underline{(R_3NH)_2X} + 2\,H^+ + Cr_2O_7^{2-} \rightleftharpoons \underline{(R_3NH)_2Cr_2O_7} + 2H^+ + X^{2-}$$

Acid stripping:

$$\underline{(R_3NH)_2Cr_2O_7} + 2\,H^+ + X^{2-} \rightleftharpoons \underline{(R_3NH)_2X} + 2H^+ + Cr_2O_7^{2-}$$

Kitagawa *et al.* (1977) believed that both mechanisms could be used successfully in ELMs. But Hirato *et al.* (1990) found that the co-transport type extraction could give far better results in comparison with counter-transport, which they demonstrated for extraction of U (VI) and Mo (VI) by using tri-n-octylamine in ELM systems.

There is considerable amount of interest in ion pair extractants, even though amine systems tend to be more complicated than chelating systems. The interest stems from the following reasons:

- The large number of aqueous anionic systems where an amine extractant may be applicable.
- The large variety of potential stripping agents as compared for example, to copper loaded chelates, where stripping with sulfuric acid is the norm.
- The three variables: pH, the oxidation state of the metal and the concentration of the anion contributing to the anionic metal complex, all of which are important in metal separation schemes with amines.

Amine extractants remain an inviting option for metal anion extraction into ELM systems and considerable amount of effort is put in this area by various investigators to develop best conditions for the extraction, stripping and final product recovery.

2.6.3 Neutral or solvating carriers

Extractants/ Carriers of this class are basic in nature and will coordinate to certain neutral metal complexes by replacing water of hydration, thereby causing the resulting organo-metal complex to become aqueous insoluble but organic soluble. Extraction by solvation requires the transfer of a formally neutral species from the aqueous to the organic phase by solvation of the hydrogen ion of a complex metal acid species or by solvation of the metal ion of a neutral salt species. All oxygen bearing organic solvents act in this way, as will organo-phosphorous compounds such as trimesters of the phosphoric, phosphonic and phosphinic acids; alkyl phosphates; amine oxides; organo sulfoxides; and organo- sulfides (Cox and Flett 1983).

Solvating extractants have an atom capable of donating electron to a metal in the formation of an adduct, solvating power depends strongly on the basicity of the reagent and are classified according to that ability:

R_3PO > $(RO)_3PO$ > R_2CO > ROH > R_2O

tri alkyl phosphine oxides > tri alkyl phosphates > ketones > alcohols > ethers

In the carbon-bonded oxygen donor systems (eg. Ethers and ketones) water usually forms an essential part of the complex, forming a hydrogen-bonded bridge between the solvating agent and the solute. However, in the organo phosphorous systems, water is often eliminated from the organic phase. Whereas ethers, ketones and so on are all electron donating compounds, alcohols are amphoteric and exhibit both donor and acceptor properties. The physical chemistry of such extractants have been reviewed by Marcus and Kertes (1969).

In general, extractions with solvating carriers are limited by:

- The metals ability to form neutral complexes with anions
- The co extraction of acid at high acid concentrations
- The solubility of organo- metal complex in the organic carrier.

The neutral carriers that have been investigated in the emulsion liquid membrane studies are organo-phosphoryl compounds such as tri-n-butyl phosphate (TBP), tri-n butyl phosphine oxide (TBPO) and tri-n-octyl phosphine oxide (TOPO). These compounds are used extensively as carriers for the separations of actinides and lanthanides. They are especially useful for the recovery of uranium and plutonium in the spent fuel reprocessing of nuclear plants.

With regard to the physical chemistry of phosphorous bonded oxygen donor solvent, non-ideal behaviour is the rule. Hydrogen bonding type and dipole-dipole interactions are common and both self-association and carrier- diluent association complexes are well known for this class of carriers. Because of the increasing polar nature of the phosphoryl group; the solubility of the neutral organophosphorus compounds in water decreases in the following order: phosphine oxides > phosphinates > phosphonates > phosphates (Cox and Flett 1983). Low water solubility makes these reagents specially attractive for ELM applications. It is of interest to note that all the equilibrium and phase modifiers commonly used come from this class of reagents. This is no surprise since both require a group having the ability to donate electron and in some cases to be a hydrogen bond acceptor and or donor (Redbook 2001).

Reusch and Cussler (1973) introduced the use of macrocyclic compounds as metal carriers in emulsion liquid membranes. Macrocyclic ligands include crown ethers and their derivatives. These compounds are cyclic or polycyclic organic molecules that contain heteroatoms capable of forming electron rich interior cavities. Such compounds posses the ability to complex ions or molecules in the electron rich cavity via ion-dipole or dipole-dipole interactions. When these macrocyclic molecules are incorporated as carriers into liquid membranes the flux of different species can differ enormously. Reusch and Cussler found that the flux of potassium ions through a liquid membrane containing dibenzo-18-crown-6 ether was 4000 times higher than the flux of lithium ions.

In recent years Izatt, Christensen and their coworkers undertook a systematic study to facilitate the transport of several alkali, alkaline earth and transition metal cations using macrocyclic carriers in ELMs (Christensen *et al.* 1983; Izatt *et al.* 1986,1987). Keeping in view that separations among the alkali, alkaline earth and trivalent lanthanide and actinide cations have traditionally been difficult to achieve, emulsion membranes containing macrocyclic ligand carriers offer a viable alternative for selective separation of these cations.

2.6.4 Copper extraction using emulsion liquid membranes:

Ever since its inception ELMs have been tried out for the removal of variety of metal anions and cations from aqueous streams. Earliest investigations on metal extraction from aqueous streams were all targeted towards the removal of Cu (II) and other bivalent cations of heavy metals. Although Strezelbici *et al.* (1978) used D2EHPA as carrier in ELMs for copper extraction but most investigators preferred to use chelating carriers. Frankenfeld and Li (1977), Kitagawa *et al.* (1977), Cahn and Li (1978), Lee, Evans and Cussler (1978) were among the earliest investigators to report the extraction of copper using ELMs with LIX reagents as carrier.

Volkel, Halwachs and Schugerl (1980) extracted Cu^{2+} at 2 pH, with initial concentrations ranging from 1000 mg/L to 100 mg/L using ELMs made from kerosene containing LIX 64N as carrier and Span 80 as emulsifier. Stripping was achieved by H_2SO_4 in the internal phase (0.25M to 2.3M). They report up to 98% Cu extraction at feed/emulsion ratio of 13:1; copper ions could be enriched within the stripping phase up to a ratio of 500:1. A mass transfer model was presented that described the kinetics of copper removal and mass transfer coefficient k_La was determined using this model. Marr and Kopp (1980,1982) also used LIX 64N as carrier to concentrate copper in ELMs these investigators also used stearic acid as carrier in ELMs for copper extraction. They report that for extraction using stearic acid as carrier the feed phase should have $pH > 4$ while with LIX 64N the feed pH should be greater than 1.8.

Frankenfeld, Cahn and Li (1981) also used ELMs containing LIX 64N as carrier for copper extraction. S 100N was chosen as the membrane phase and a polyamine surfactant was used. Variables governing the permeation of copper ions through the liquid membrane like carrier concentration, emulsion/ feed ratio and internal phase concentration were studied. Economic evaluation shows that the ELM process is 40% cheaper than solvent extraction. The separation results used in the economic evaluation were from a continuous run conducted at Davy McKee Co in UK that lasted 9 days. Real leach liquor was employed. Copper extraction of 92% was obtained after 10 minutes residence time of the liquor in the extractor. The liquid membrane selectivity of Cu vs. Fe during extraction was good, with an average of 130. The main savings stemmed out of reduction in number of stages and reduction of the costly organic inventory.

An interesting study reporting the effect of emulsifier type on copper extraction using ELMs containing LIX 65N-LIX 63 mixtures was done by Mikucki and Osseo-Asare (1986). They used four different emulsifiers Span 80 (sorbitan monooleate), Arlacel 83 (sorbitan mono and dioleate), Span85 (sorbitan trioleate) and Brij 72 (polyoxyethylene 2 stearyl ether). Their findings indicate that interfacial activity of the emulsifiers increased in the order Brij 72 $<$ Span 85 $\ll$ Arlacel 83 $\simeq$ Span 80. The emulsifier concentration required for achieving good stability varied widely with emulsifier type being minimum with Span 80. Further these investigators observed that copper extraction passed through a maximum and then decreased as the emulsifier concentration was increased. The initial increase was attributed to decrease in membrane breakdown. The subsequent decrease in extraction they attributed to a number of factors including a decrease in the rate of copper complexation at the membrane phase / external phase interface, an increase in interfacial viscosity, a decrease in movement of internal phase droplets within the emulsion globules and a decrease in the external interfacial area available for metal extraction. These investigators conclude that the smaller the concentration of emulsifier necessary in order to achieve good membrane stability, the better the metal extraction.

Nakashio *et al.* (1988) also studied the influence of the surfactant on ELM separations. They extracted copper using LIX 65N as carrier and n-heptane as the membrane phase. The surfactants tried out were Span 80, polyamine and glutamic acid dioleyl esters, they found glutamic acid esters to be superior to the other two surfactants in terms of membrane stability and demulsification behaviour Chakravarti *et al.* (2000) separated Cu^{2+} ions from simulated wastewaters using ELMs containing LIX 622 as carrier also with LIX 84 as carrier. They reported the interference of Cd^{2+}, Ni^{2+} and Zn^{2+} on the transport of Cu^{2+} ions.

Although LIX reagents have been widely used as carriers for copper extraction using ELMs some investigators have also used chemically identical reagents (chelating carriers) marketed by Shell and ICI (Acorga). Martin and Davies (1977) used emulsion liquid membranes with SME 529 (Shell) as carrier, Shellsol as the membrane material and Span 80 as emulsifier to recover copper from dilute aqueous solutions in batch and semi continuous operations. A solution of 200g of H_2SO_4 per liter containing additionally up to 20,000 mg/L Cu^{2+} was used as a stripping solution. Under these conditions mass transfer was achieved from a feed solution of 120 mg/L into a stripping solution containing more than 20,000 mg/L Cu^{2+} clearly a case of uphill transport.

Teramoto *et al.* (1983) obtained experimental data on batch extraction of copper by emulsion liquid membranes using SME 529 as a carrier. The data were analyzed on the basis of a general permeation model in which diffusion in the W/O emulsion drop, external mass transfer around the drop, rates of formation as well as decomposition of the copper-carrier complex at the aqueous / water interface and the leakage of the internal phase to the external phase due to membrane breakage were taken into account.

Bart *et al.* (1988) studied extraction of copper with ELMs in continuous columns. Emulsions were prepared from Shellsol T using Paranox 100 as surfactant. The carrier used was P 50 (Acorga Ltd.). Copper concentration profile in the column was measured and a mass transfer model was developed that described column performance in a kinetically controlled regime.

In recent years perhaps the most interesting and encouraging study of copper extraction using ELMs was reported by Wright *et al.* (1995). The investigation was carried out by the U.S. Bureau of Mines for the extraction of copper from heap-leach and mine solutions with the objective of developing innovative water purification technology. A nine-day around-the-clock test was performed in a copper mine in Arizona during which 5600 gallon of solution was processed. Three different solutions were used during the tests. They were (1) normal plant pregnant leach liquor (PLS) containing 1.43 g/L Cu, (2) PLS diluted with mine water to 500 mg/L Cu, (3) PLS diluted with mine water to 320 mg/L Cu. All three solutions contained suspended solids that did not adversely affect the ELM system. The emulsions were prepared using Isopar as the membrane phase, Paranox 100 emulsifier, and Acorga M5640 as the carrier. Internal phase contained 20g/L Cu and 165 g/L H_2SO_4. In all three cases extraction of Cu exceeded 92%. The authors have indicated that future USBM ELM research will focus on recovering copper from dilute solutions and at lower pH (below 2.0).

2.6.5 Metal extraction using emulsion liquid membranes.

Metal extraction from aqueous systems appears to be the area of primary interest of most investigators working in the field of ELM technology. Almost all metals including rare earths and nuclear metals have been investigated to some extent although focus was more on copper extraction. Ho and Sirkar (1992); and Bartsch and Douglas Way (1996) present a comprehensive review of metal separations by ELMs.

A brief summary of some interesting and pioneering studies other than that for copper extraction is reported herewith.

Arsenic: Huang *et al.* (1996) studied arsenic removal from metallurgical wastewater by ELMs formulated from n-heptane containing 10 %(vol.) 2-ethyl hexyl alcohol as carrier with ECA 4360 J as emulsifier. NaOH was used as the internal stripping media. The concentration of arsenic was removed from 5.51 mg/L to less than 0.25 mg/L within a time span of 30 minutes.

Cadmium: Frankenfeld and Li (1977) studied cadmium removal from metal plating baths using ELMs containing Aliquat 336 as the carrier. They observed that stripping was quite difficult due to the stability of Cd $(CN)_4^{2-}$ complex under basic conditions. Stripping could be achieved successfully only by using EDTA in the pH range of 4 to 6 in the internal phase.

Marr and Draxler (1992) demonstrated the removal of cadmium and other heavy metals in their pilot plant operations with 99% efficiency using ELMs containing Di (2-ethyl hexyl) thiophosphoric acid as carrier. In recent years Quan-Min-Li (1997,1998) studied the transport of Cd^{2+} ions through ELMs containing trioctylamine as carrier in order to separate cadmium from zinc, iron, cobalt and nickel containing solutions. Gabriel Sznejer and Marmur (1999) removed Cd^{2+} ions from aqueous streams using diethyl hexyl phosphoric acid carrier in emulsion membranes prepared from paraffin oil with Span 80 as emulsifier. They concluded that the main resistance to mass transfer centered in the outer oil/water interface since the separation process was independent of the W/O phase ratio that controls inner interfacial area and the membrane thickness.

Urtiaga *et al.* (2000) made a comparative study of Cd^{2+} removal by ELM process with that of supported liquid membranes and non-dispersive solvent extraction using Cyanex 302 as carrier. The rate of Cd^{2+} removal varied in the order: NDSX > ELM > SLM.

Cesium: El-Said *et al.* (2003) investigated the permeation of cesium (Cs 137) from nitrate solutions with ELMs containing crown ether (18-crown 6) as carrier, xylene as membrane phase and Span 80 as carrier. Ephidrine was used as stripping agent. The extraction rates were influenced by the ionization constants of ephedrine hydrochloride at different pH.

Chromium: Hochhauser and Cussler (1975) were the first to demonstrate chromium extraction as dichromate ($Cr_2O_7^{2-}$) into emulsion liquid membranes by the co-transport mechanism using dodecyl amine as carrier. Dichromate ion was also extracted by Alamine 336 - Span 80 – Isoparaffin ELM system by Kitagawa *et al.* (1977); TOA –LMS 2 – Kerosene ELMs by Zhang *et al.* (1988), TBP – Span 80 – n-Hexane ELMs by Vohra *et al.* (1989). In all the above-mentioned investigations NaOH was used as the stripping phase.

Fuller and Li (1984) analyzed extraction of chromium (IV) from cooling tower effluents by ELMs containing Aliquat 336 as carrier and nonyl- decyl alcohols for the solubilization of the complex in the membrane phase. Mori *et al.* (1990) used ELMs containing tri-n-octylamine carrier, Span 80 /ECA 4360 as emulsifiers and LiOH as stripping reagents in the recovery and concentration of Cr(VI) from aqueous sulfuric acid solutions. Salazar *et al.* (1990, 1992) investigated the influence of membrane composition and surfactant on the recovery of Cr(VI) from sulfuric acid baths employed in electroplating processes. Chakravarti *et al.* (1995) studied the influence of stripping phase reagent type and its concentration on the extraction of Cr (VI) from simulated wastewaters using Aliquat 336 - Span 80 – Kerosene + Paraffin ELMs.

Recently Banerjea, Dutta and Sanyal. (2000) developed mathematical model for batch extraction of Cr (VI) from aqueous acidic solution using Aliquat 336- Paranox 106-Kerosene ELMs with NaOH as strippant. and decanol as stabilizer. The model assumed instantaneous and irreversible reaction at membrane-internal droplet interface. Bhowal and Dutta (2001) further extended this model to include simultaneous reactions of quaternary ammonium salt with Cr (VI) and hydroxyl anions in the aqueous phase. Moreover, these investigators considered reversible reactions that are more realistic in comparison with irreversible reactions.

Cobalt: Strzelbicki and Charewicz (1978) studied the extraction of cobalt from aqueous solution of nitrate salts at pH 3.1 using ELMs containing D2EHPA as carrier.

The membrane phase was cyclohexane and Span 80 was used as the emulsifier the internal stripping phase was 2M HNO_3. Effect of pH, surfactant concentration and rate of stirring on cobalt extraction were studied. These investigators achieved almost 99% cobalt recovery.

In a later work Strzelbicki and Charewicz (1980) studied the effect of carriers on the separation of Cu^{2+}, Co^{2+} and Ni^{2+} from aqueous mixtures using Span 80 – Kerosene ELMs. They observed separation factors were very sensitive to pH and obtained the following separation factors at pH of 2.25 with D2EHPA as carrier for extraction of metal nitrates from aqueous solutions: Cu/Co = 70.8; Cu/Ni = 228; and Co/Ni = 3.22. At pH 3.36 the separation factors dropped dramatically to give Cu/Co =1; Cu/Ni = 1.17; and Co/Ni = 1.17. Strzelbicki and Schlosser (1989) studied the influence of surfactants on the transport of Co^{2+} cation through ELMs containing D2EHPA as carrier. They found that extraction rates were superior using Span 80 in comparison with ECA 4360 and Paranox 100.

Mercury: Frankenfeld and Li (1977) were the first to report the extraction of mercury using ELMs containing quaternary ammonium salts as carrier. They could reduce the mercury (Hg^{2+}) content from 1100 mg/L down to 0.3 mg/L in 10 minutes. Weiss *et al.* (1982) using dibutylbenzothio urea as carrier in ELMs reduced mercury content in aqueous streams by 95 % within 3 minutes. Boyadzhiev *et al.* (1983) extracted mercury cations from low pH aqueous solutions using ELMs that were prepared from n- paraffin's containing 10% oleic and linolic acids they could achieve 1000 fold increase of metal in the receiving encapsulated phase.

Larson *et al.* (1994) investigated mercury extraction using coarse W/O emulsions as well as microemulsions as ELMs. The Sauter mean diameter reported for microemulsions was 0.014 mm to 0.017 mm as compared to 0.5 to 1mm for coarse emulsions. They developed a diffusion model for mercury extraction using microemulsions and showed that the mechanism of extraction using microemulsions is similar to that of macroemulsions.

Molybdenum: Kulkarni and Mahajani (2002) investigated the extraction of molybdenum using ELMs containing Aliquat 336 as carrier. Mixed xylenes, dodecane, heptane and kerosene were tried out as membrane phase and Monesan was used as the emulsifier. NaOH was the stripping reagent. It was observed that the extraction and enrichment was found to decrease in the order: dodecane > kerosene > heptane > xylenes. Maximum extraction was reported when internal phase concentration of caustic was 500 mol/m^3 and pH of feed phase was 4.

Nickel: Marr and Draxler (1992) recovered nickel from wastewaters from electroplating industry with 99.8% efficiency using ELMs containing Di(2-ethylhexyl) dithiphosphoric acid (DTPA) as carrier, ECA11522 polyamine surfactant and Shellsol T as membrane phase. Juang and Jiang (1995) studied the possibility of nickel recovery from Watts Nickel bath rinse solutions using ELMs containing D2EHPA carrier. The membrane material was n-heptane and emulsifier used was Span 80. 1 M H_2SO_4 was used as internal stripping phase. Nickel recovery in this ELM system reached about 425 per stage. These investigators found that the volume fraction of the internal phase and treat ratios to be the most important parameters in determining the recovery factor of Nickel.

Kulkarni *et al.* (2001) extracted nickel in ELMs containing D2EHPA as carrier. They used methane sulfonic acid as stripping agent and observed that methane sulfonic acid to be a superior stripping agent in comparison to mineral acids. Further they found that decane was a better membrane material for nickel extraction in ELMs, in comparison with heptane, toluene and xylene.

Chakraborty *et al.* (2003) investigated the influence of ELM globule size distribution on nickel extraction using D2EHPA carrier. They found that polydisperse effects had very little influence on mass transfer behavior.

Precious metals: Gold, silver and palladium have also been extracted using ELMs. Lee *et al.* (1996) have reported silver extraction using emulsion liquid membranes. Yan *et al.* (1990) were the first investigators to extract gold using ELMs. Recently Kargari *et al.* (2004 a, 2004 b) investigated extraction of gold using ELMs containing methyl-isobutyl ketone as carrier and biodegradable LK-80 (a complex mixture of esters and polyesters) as emulsifier and liquid paraffin as the membrane phase. Sodium sulfite and sodium hydroxide mixture was used as the stripping reagent almost complete recoveries were obtained in a span of 25 minutes under optimized operating conditions.

Kakoi *et al.* recovered palladium from acidic solutions of high iron concentrations using ELMs containing di(2-ethyl hexyl)monothiophosphoric acid as carrier. The concentration of thiourea used as stripping agent greatly affected the efficiency of palladium recovery. Extractions were carried out in batch as well as in continuous mixer settler systems.

Rare earths: A number of investigators have attempted to recover rare earth metals from aqueous solutions. Yu *et al.* (1982) separated Europium using ELMs, Brown *et al.* (19830 also studied europium transport in ELMs using macrocyclic polyether 18-crown-6. Teramoto *et al.* (1986), Tang and Wai (1989), Zhang and Wang (1989), Reihua and Dexian (1989), Uezu *et al.*(1995,1997) and Kakoi *et al.* (1997) all investigated extraction of rare earths using ELMs.

Goto *et al.* (1993) extracted lanthanum, praseodymium and neodymium using ELMs containing PC-88A as carrier and heptane as membrane phase. They investigated the effect of surfactant nature on extraction behavior and found that synthesized cationic surfactant accelerated the extraction rate of rare earths in comparison with the non-ionic Span 80 and PX-100.

Lee *et al.* (1994) reported the transport of Eu (III) from dilute aqueous streams with ELMs prepared from three potential carriers HDEHP, PC-88A and CYANEX 272. They also studied the effect of three diluents xylene, n-dodecane and kerosene on europium extraction and suggested an optimal combination for maximization of separation

Selenium: Gleason *et al.* (1996) investigated the removal of selenium from contaminated waters using ELMs. Kerosene was used as the membrane phase with n-decanol as the co solvent but the emulsifier and the carrier used were proprietary. Internal phase was NaCl solutions (0.5 to2M). The investigators found that Se(VI) (selenate) was extracted more rapidly than Se(IV) (selenite) and the extraction rate of Se(IV) was very sensitive to pH. Effect of various process parameters on extraction was studied. Batch extractions as well as continuous column extractions were performed and selenium concentrations were reduced from 1mg/L to a level below 0.01 mg/L within 15 minutes of contact time.

Tellurium: Chakraborty and Dutta (1996) extracted Te (IV) from its acidic solutions using ELMs containing D2EHPA as carrier and kerosene as the membrane phase. Effect of various parameters such as feed concentration, extractant concentration, speed of agitation etc were studied. Results showed that with proper adjustment of experimental conditions the rate of extraction through the membrane could be enhanced.

Uranium and other Radioactive metals: Block and Valint (1982) extracted uranium from wet phosphoric acid using D2EHPA-TOPO mixed carrier with LOPS as membrane phase and PIBSA-polyamine surfactant. Hayworth (1983) studied the same system and reported 90% extraction. Hirato *et al.* (1991) concentrated uranyl sulfate with tri-n-octylamine - Span80 - kerosene liquid membranes using 1M Na_2CO_3 as stripping agent. They extracted 95 % of uranium existing in the feed solution. El-Reefy *et al.* (1997,1998) reported the equilibrium and kinetic studies of uranium and thorium extraction from nitric acid and hydrochloric acid medium using ELMs containing TOPO as carrier.

Recently Kulkarni *et al.* (2002) presented an extensive study on separation and recovery of U (VI) from aqueous solutions using ELMs containing TOPO as carrier, paraffin as membrane phase and Span 80 as emulsifier. Na_2CO_3 was used as the internal stripping phase; they observed that stripping phase concentration of 0.5M gave maximum uranium recovery. Further these investigators observed that presence of iron in the aqueous stream was deleterious to uranium extraction. They reported that on an average uranium extraction decreased by 25% in the presence of iron. M.S.El Sayed (2003) extracted uranium from gattar sulfate leach liquor using Aliquat 336- Span 80 – kerosene ELMs containing 1M Na_2CO_3 as stripping agent and reported the effect of various parameters on the rates of extraction.

Eroglu *et al.* (1993) used ELMs to extract strontium ions. The ELM system was D2EHPA – Span 80 – kerosene. Stripping phase was HCl at 1.6 pH, while the external pH was maintained at 5.3. A maximum of 92 % extraction is reported with extraction efficiency increasing with increase in treat ratio, stirring rate, D2EHPA concentration and decrease in inner phase pH.

Zinc: Extraction of zinc from wastewaters of synthetic fiber industry was the first commercial scale application of emulsion liquid membrane technology. Investigations and initiative of Marr and coworkers (1988a, 1988b, 1992) was responsible for the erection of this plant by Lenzig AG in the Austrian viscose and rayon industry. Wastewaters coming from spinning bath containing about 500 mg/L of Zn were treated with ELMs and the zinc ions were separated selectively from calcium present in the water stream and brought down to less than 3 mg/L. Several other processes such as precipitation, ion exchange resins and solvent extraction were explored but ELM permeation proved to be the most economic.

Initially a pilot plant with throughput of 1m^3/h capacity was constructed; a major problem in the operation of the pilot plant was the choice of a suitable carrier. D2EHPA is commonly used for zinc extraction in hydrometallurgical industry, but selectivity of this extractant to calcium was not sufficient in this case. Cyanex 272 and PC-88A had the required selectivity but the extraction efficiency was too small at the given pH values. Only use of bis (2-ethylhexyl) dithiophosphoric acid (DTPA) made it possible to solve the problem in a satisfactory manner.

After two years of successful operation of the pilot plant the main plant was erected that had a capacity of 75 m^3/h. The mass transfer equipment used was countercurrent permeation column having 1.6m diameter and an effective height of 10m, its internals resemble an Oldshue-Rushton column. The following optimal operating conditions were arrived after months of operation:

Wastewater 70 m^3/h: Initial Zn conc.: 350mg/L
Final Zn conc.: 5 mg/L

Membrane phase Shellsol T 7 m^3/h
Stripping phase 0.3 m^3/h Initial conc. H_2SO_4: 250 g/L
Final conc. H_2SO_4: 100 g/L Zn 55 – 60 g/L

Surfactant initially used was PX 100, but due to bacterial damage of the surfactant in one month's operation a bacteria resistant surfactant required to be used.
Lobrach and Marr (1987) presented the modeling of zinc extraction using ELMs with DTPA as carrier, Yu *et al.*(1987) also reported Zn extraction using ELMs in Oldshue-Rushton columns. Ortiz Uribe *et al.*(1988) extracted zinc from sulfate solutions in a spray column using ELMs they identified four different controlling regimes depending on range of concentration of species and hydrodynamic conditions in the extractor. Goto et al (1991) tried out glutamic acid esters as surfactants for zinc removal using ELMs containing PC-88A. Bart *et al.* (1992) investigated the osmotic swelling behavior of ELMs during zinc extraction using bis (2 –ethyl hexyl) monothiophosphoric acid.

Carvalho and coworkers (1993a, 1993b, 1994) investigated zinc extraction from sulfate solutions using ELMs containing monothioDEHPA and dithioDEHPA. They noticed that measuring dynamic interfacial tensions was a useful technique to follow the degradation of reagents and interpret some kinetic data. Later Reis and Carvalho (2004) extended the Lobrach and Marr model and accounted for the transient diffusion of solutes within the emulsion globule.

Multicomponent extractions: A number of investigators studied the extraction of metal ions from multicomponent mixtures using ELMs. Strzelbicki and Charewicz (1980) studied separation of copper, cobalt and nickel from their mixtures using various carriers, Fuller and Li (1984) reported the separation of Cr (VI), Cr(III) and Zn from cooling tower blow down streams using ELMs. Izzat *et al.* (1987) studied the separation of Cd (II), Hg(II) and Zn(II) using ELMs containing crown ethers. Marr and coworkers (1988a, 1988b) carried out pilot plant studies for extraction of zinc, copper, nickel, cadmium, lead and chromium from mixtures. Longquan *et al.* (1997) separated cobalt and nickel using EDTA as masking agent. Recently Okamoto *et al.* (2000) used ELMs containing PC-88A to extract metal ions such as Cr(III), Mg(II), Co(II), Ni(II), Cu(II) and Cd(II) from trace concentrations in solutions.

2.6.6 Biochemical and other applications

Potential ELM applications in biochemical processing include separation of amino acids, biochemicals and penicillin G from fermentation broths. Teramoto *et al.* (1991) carried out batch extraction of tryptophan and phenylalanine using ELMs containing D2EHPA as carrier. Hong *et al.* (1992), Itoh *et al.*(1990) also extracted phenylalanine at pH 2.5 using ELMs containing D2EHPA as carrier, the extraction efficiency is reported to be 80%.

Chaudhuri and Pyle (1992) extracted lactic acid with ELMs containing Alamine 336 as carrier and studied the effect of Span 80 and carrier on system stability. Reisenger and Marr (1993) compared the separation of lactic acid and L-Leucine using ELMs. The carrier used for lactic acid was Amberlite LA-2 and for L-Leucine was Aliquat 336. They showed that lactic acid permeation was controlled by rate of reaction while L-Leucine permeation was controlled by rate of reaction and diffusion through the emulsion globule.

Extraction of Penicillin-G with ELMs was first studied by Hano *et al.* (1990, 1993) in batch as well as in continuous systems. Lee and coworkers (1992, 1994, 1996, 1997, 1998) extensively studied the extraction of Penicillin-G in ELMs prepared using kerosene as the membrane phase, Amberlite LA-2 as the carrier and ECA 4360J as the surfactant. Sodium carbonate was used as the stripping agent. Penicillin was extracted from citrate buffer at pH 5 in batch as well as continuous countercurrent column of the Oldshue-Rushton type. Almost 90 % recovery is reported and a mathematical model was developed that predicted the effect of various parameters on extraction rates with reasonable degree of accuracy.

The transport of anions such as chloride, cyanide, sulfate, phosphate etc. into ELMs were also been studied by numerous investigators notable among them are Schiffer *et al.* (1974), Frankenfeld and Li (1977), and Cussler and Evans (1980). In most cases trioctylamines were used as carriers. Cyanide removal from waste liquors in gold processing is being commercialized at the Huang-hua mountain gold plant near Tianjin, China.

2.7 SUMMARY

Detailed literature survey on the Emulsion liquid membrane separation technique reveals the following:

i. The emulsion liquid membrane separation process is a very promising separation technique on account of its inherent simplicity, ease of implementation and rapidity of separations coupled with diversity of applications.

ii. The widest range of applications of ELM technique lies in the area of solute extraction from aqueous streams using W/O emulsions. Although selective separation of organic solutes from organic streams using O/W emulsions can also be achieved.

iii. In view of the possibility of selecting membrane material, surfactant and carrier from a very wide range of products available commercially that fulfill the functional requirements, there exists a vast diversity of emulsion systems that have been used. The variety of methods and equipment used for preparing emulsions also add to the diversity. Such diversity on one hand provides numerous alternatives that may be capitalized on to develop viable separation systems while on the other hand it tends to inhibit the possibility of standardization of procedures. Increasingly it appears that investigators are preferring kerosene as membrane material and Span 80 as emulsifier to prepare the W/O emulsions. However, there is a continual search for superior emulsifiers.

iv. Most of the investigations done in this field are exploratory in nature, with the objective to establish the possibility of separation of specific solute/solutes from aqueous solutions using ELMs. With the exception of select few, none of the investigators have provided any characterization of the emulsions used. Very few have commented on aspects of emulsion stability during operations. Emulsion swelling, leakage/breakage have been recognized by most investigators but only few have tried to categorize them.

v. Phenol has been the solute of interest in separations using the Type I facilitated transport mechanism, and has been widely studied. However, with the exception of two investigations that of Chang and Li (1983) and Kataoka *et al.* (1989), none reported the effect of internal phase variation ϕ on extraction.

Further, even the effect of treat ratios has not been widely investigated. Moreover, investigators who studied the effect of treat ratios in batch extraction systems did not retain constant molar ratios (*M*) of the external solute phase with that of internal reagent phase, thereby introducing noise in the data. It is felt more focused investigation is necessary to overcome this lacuna.

vi. There is very limited information available on extraction of other phenols such as cresols, chlorophenols etc. using ELMs. It would be presumptuous to expect that all phenolic compounds will show identical extraction behaviour as that of phenol. Comprehensive experimental data is required to establish the extraction behavior of these compounds using ELMs. It would therefore be appropriate to investigate phenol extraction and also extraction of other phenols such as cresols, chlorophenols etc. using adequately characterized ELMs. Such data will not only provide inputs for obtaining recipes of ELMs for maximization of removal rates but also serve as foundation for developing process design correlations and methodology in future.

vii. Extraction of solutes using the Type II facilitated transport mechanism has been widely investigated in ELM systems. Focus of such separations has been primarily on metal extractions however; numerous other solutes such as amino acids, antibiotics have also been studied. Although copper extraction from sulfate media is well investigated using ELMs containing chelating carriers, but there still exists considerable scope to undertake fresh investigations in this area keeping in view that most of the existing data used LIX carriers such as LIX 65N etc. which are being phased out commercially. New chelating carriers introduced in the last decade such as LIX 984NC have not been explored using ELMs. Further extractions at pH lower than pH 2 have not been investigated at all using ELMs. These aspects need to be addressed in order to consolidate the wealth of information available on copper extraction in ELMs.

viii. Extraction of copper from ammoniacal leach solutions is becoming increasingly popular since ammoniacal leaching offers the possibility of hydrometallurgical treatment of copper sulfide ores and copper scrap. Chelating type carriers such as LIX 84 have been used in solvent extraction of copper from ammoniacal solutions but till date extraction of copper from ammoniacal media using ELMs have not been investigated. This area provides ample challenge and opportunities for exploitation using ELMs.

ix. There is limited information on extraction of nickel using ELMs. Moreover, only D2EHPA was used as carrier by investigators. In hydrometallurgy, chelating carriers are being increasingly used to extract nickel from ammoniacal media and it is worthwhile to explore the possibility of nickel extraction using chelating carriers.

x. Continuous scale operations, demulsification and membrane recycling need to be investigated with greater vigour since these aspects of ELMs are not very well studied. Emulsion liquid membrane technology is still in its nascent state of development while the applications are endless. However, in order to mature out as a separation process it still has a very long way to go and many a challenge to overcome.