In the present research project, it is aimed at studying the recovery of organic acids, namely Lactic acid, Propionic acid and Acetic acid, by using the Liquid Emulsion Membrane Technique from dilute aqueous feed solution. The major points in favor of use of LEM are its suitability for dilute feed solutions, low capital and operational costs, high % extraction, simple and fast operation and high selectivity for solutes. In the present research project, work in the following areas is required:
1. **Design of LEM** includes the selection of the constituents of the membrane phase – (organic diluent, surfactant, and carrier), and the internal stripping agent for the aqueous internal phase. This involves:

   - Equilibrium Study of various possible organic solvents for membrane formation, to select the suitable organic solvent/diluent.
   - Selection of a suitable surfactant.
   - Selection of suitable carrier for the recovery/extraction of organic acids.
   - Selection of suitable internal stripping agent.

2. **Stability analysis** for the system (membrane phase constituents and internal phase constituents) selected in the above step, is the effort in the direction of determining the value of the following parameters, (like the concentration of the stripping agent in the internal phase, the surfactant concentration, mixing ratios of emulsion and feed phase, internal phase ratio of membrane phase in emulsion formation (IPR), feed concentration), for the most stable configuration. It is desired that the emulsion should not break or leak during the extraction step under the operating conditions as this reduces the % recovery of the organic acid from the feed solutions.

3. **Extraction/Recovery study** for the three organic acids: This includes the study of effect of operating parameters, (like feed concentration change, internal stripping agent concentration change and carrier concentration change), on the rate of extraction and the % extraction achieved.

4. **Mathematical modeling** proposes a model for LEM technique, the governing mathematical equations and mathematical solutions (after making suitable assumptions) are tested by fitting the experimental values of the parameters (internal phase concentration, external phase...
concentration, mass transfer coefficient etc.) of the extraction step in the solution equation, and comparing the results thus obtained with the observed/experimental data collected during the extraction step. Graphically, a close fit between the two results validates the proposed model.

The Experimental Section of the project is thus divided into three sub-sections:

1. **Equilibrium Study**: Chemicals/equipment required, Procedure for performing and Analyzing and discussion of results.

2. **Stability Study**: Chemicals/equipment required, Procedure for performing and Analyzing and discussion of results.

3. **Extraction Study**: Chemical/equipment required, Procedure for performing and Analyzing and discussion of results.

The Experimental Section is followed by the Analytical Section, which comprises of the following:

1. **Mathematical modeling**
2. **Summary** of the entire research project.
3.1 - EXTRACTANT/CARRIER & STRIPPING AGENTS

The extractant/carrier selected should favor the distribution of the solute between the aqueous external (feed) phase and the organic membrane phase. The carrier and the carrier-solute complex should be soluble in the organic membrane phase (diluent) and should not have any solubility in the aqueous external and internal phases. It should be hydrophobic and there should be no precipitation within the membrane phase or at the interfaces. On the other hand, a stripping agent used in the aqueous internal (dispersed) phase, should favor the partitioning of the solute from the organic membrane phase to the aqueous internal phase.

According to the functional groups, extractants are generally divided into three classes:

- Acidic Extractant
- Basic Extractant
- Neutral Extractant

3.1.1 - ACIDIC EXTRACTANTS

Extraction of cationic species from an aqueous solution requires that it must be combined with an anionic species to form an uncharged species. Acidic extractants are most effective for extracting cations by exchanging
their protons with the cations from the extraction feed solution. Some commonly used acidic extractants are classified into three categories:

1. **Chelating Extractants** which include

   a) **Hydroxyoximes** such as LIX 63, LIX 64N, LIX65N, LIX 70 (*Henkel*); SME 529 (*Shell*); P17, P50 and P5050 (*Acorga*)
   
   b) **β-Hydroxyquinolines** (oximes) such as Kelex 100(*Ashland Chem*)

   c) **β-diketones** such as acetylacetone (AA) and benzoylaceton (BA)

2. **Alkylphosphorus compounds** which include

   a) **Organophosphoric acids** such as D2EHPA (di(2ethylhexyl) phosphoric acid) and DBP (dibutyl phosphoric acid);

   b) **Organophosphonic acids** such as PC88A (*Daihachi Chem Ind*), mono (2-ethylhexyl) ester of 2-ethyl Hexylphosphonic acid;

   c) **Organophosphinic acids** such as Cyanex 272 (*American Cyanamid*) di-(2,4,4-trimethyl pentyl Phosphinic acid);
d) Thiophosphoric acids such as DTPA, 
(Hoechst) di (2-ethyl hexyl) dithio 
phosphoric acid

e) Thiophosphinic acids such as Cyanex 301, 
(American Cyanamid) di-(2,2,4-
trimethylphenyl) dithio phosphinic acid

3. Ionizable crown ethers such as crown ether carboxylic acid, 
crown ether phosphonic acid mono alkyl ester (Bartsch et al\textsuperscript{44} 
243 (1987), and naturally derived antibiotic macrocycles such as 
monesin (Cussler and Evans\textsuperscript{43} (1974).

In general, the coordination complex of the chelating 
extractant with positively charged metal ions is very specific, which results in the 
selective separation of metals. Alkyl phosphorus compounds are less selective, 
less expensive, more soluble than metal chelates in organic solvents, therefore 
they are widely used in hydrometallurgical extraction processes. These are also 
called liquid cation exchangers.

The extraction and stripping reactions for solute transport 
across the membrane by an acid extractant can be represented as:

**Extraction:** F/S interface

\[
\begin{align*}
M^{2+} & \hspace{1cm} + \hspace{1cm} 2HR & \rightarrow & \hspace{1cm} MR_2 & + & \hspace{1cm} 2\text{ H}^+ \\
\text{Aqueous} & \hspace{1cm} \text{organic} & \hspace{1cm} \text{organic} & \hspace{1cm} \text{aqueous} & \hspace{1cm} \text{Phase} & \hspace{1cm} \text{phase} & \hspace{1cm} \text{phase}
\end{align*}
\]
HR is the protonated form of an acidic extractant, $M^{2+}$ is the metal ion and $H^+$ the hydrogen ion. Proton is the driving force, which pumps the metal ion against its own concentration gradient between the external and internal phases.

3.1.2 - BASIC EXTRACTANTS

Basic extractants can be of various types: High molecular weight primary amines such as Primene JMT, secondary amines such as Amberlite LA-2, tertiary amines such as trioctylamine TOA, tri-n-octylamine TNOA and Alamine 336, and quarternary alkylammonium salts such as Aliquat 336 are used for the extraction of anionic or neutral metal complexes ($\text{Cd(CN)}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{AuCl}_4^-$, $\text{UO}_2(\text{SO}_4)_2^{2-}$) and organic acids (Lactic acid, Propionic acid, acetic acid). They are known as liquid anion exchangers. Primary and secondary amines show poor stability and are not used. Tertiary amines are the most widely used basic extractants. Quarternary salts are used for high pH feed solution extraction. The extraction using tertiary amines follow two possible mechanisms depending on the stripping agent in the internal phase:

Co-transport: If a basic solution is used as a stripping agent in the internal phase, the permeation of metal anions proceeds according to the co-transport
mechanism, in which the transport of the metal anion (A') across the membrane is coupled to the transport of hydrogen ion (H+) in the same direction with the following reactions.

**Extraction:** F/S interface

\[ R_3N + H^+ + A^- \rightarrow R_3NHA \]

Organic phase Aqueous phase Organic phase

**Stripping:** S/R interface

\[ R_3NHA + Na^+ + OH^- \rightarrow R_3N + Na^+ + H_2O \]

Organic phase Aqueous phase Organic phase Aqueous phase

**Counter-transport:** If an acid serves as the stripping agent in the internal phase, the permeation of metal anions obeys the counter transport mechanism, and metal anions are transported in the direction opposite to the coupled anions with the following extraction and the stripping reactions. \( R_3NHX \) is the amine salt, \( A^- \) is anion, and \( X^- \) is coupled anion.

**Extraction:** F/S interface

\[ R_3NHX + H^+ + A^- \rightarrow R_3NHA + H^+ + X^- \]

Organic phase Aqueous phase Organic phase Aqueous phase

**Stripping:** S/R interface

\[ R_3NHA + H^+ + X^- \rightarrow R_3NHX + H^+ + A^- \]

Organic phase Aqueous phase Organic phase Aqueous phase
Neutral extractants often extract uncharged metal complexes or cations together with coupled anions in order to maintain the electric neutrality. In this type of extraction the metal species is coordinated with two different types of ligands, i.e., a water-soluble anions and an organic-soluble electron-donating functional group. Most of the neutral extractants that have been investigated in the liquid membranes are *organo-phosphoryl compounds* such as TBP (tri-butyl phosphate), tri-n-butylphosphine oxide (TBPO), and tri-n-octylphosphine oxide (TOPO). These compounds are used for separation of lanthanides and actinides, and for recovery of uranium and plutonium in nuclear plants.

**Extraction**: F/S interface

\[ M^+ + A^- + L \rightarrow ML \]

Aqueous phase \hspace{1cm} Organic phase \hspace{1cm} Organic phase

**Stripping**: S/R interface

\[ MLA + Ms^{+} + R^- \rightarrow L + MR + Ms^{+} + A^- \]

Organic phase \hspace{1cm} Aqueous phase \hspace{1cm} Organic phase \hspace{1cm} Organic phase

Where,

\( M^+ \) is metal ion, \( A^- \) is the co-anion, \( Ms^{+} \) is co-cation, \( L \) is the neutral extractant, \( R^- \) is the anion.

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

3.2 – SURFACTANTS

A surfactant is a key component in the formation of a stable emulsion. In LEM study the majority of the systems studied are the type W/O/W double emulsions in which an oil soluble surfactant is required with properties favoring the above type of emulsion system. A surfactant should possess the following properties:

1. It does not react with the extractant in the membrane phase, and if there is any reaction it should promote the extraction process rather than catalyze the decomposition of the extractant.

2. It has a low interfacial resistance to mass transfer.

3. It does not inhibit demulsification.

4. It should be soluble in the membrane phase but not soluble in the external and the internal phases.
5. It is stable against acids, alkali and bacteria.

6. It should be cheap and non-toxic.

**SPAN 80 (sorbitan monooleate)** is a non-ionic surfactant, with molecular weight 428 and structure:

\[
\begin{align*}
&\text{O} \\
\| & \\
\text{CH}_3(\text{CH}_2)_7 - \text{CH} - (\text{CH}_2)_7 - \text{C} - \text{O} - \text{CH}_2 \\
&\text{OH} \\
&\text{OH} \\
&\text{OH}
\end{align*}
\]

The commercial sample of SPAN80 has small impurities of di and tri oleates (Goto et al. 231(1987), Nakashio et al. 232(1988). The membranes having SPAN80 as surfactant show less mass transfer resistance as compared to other surfactants (Draxler and Marr 69(1986), Strzelbicki and Schlosser 123(1989), Lee and Chan 63 (1990)). It has a drawback, however that it is a good carrier for water molecules and therefore favors the osmotic swelling of emulsions (Martin and Davis 99(1977), Colinart et al. 233(1984), Draxler and Marr 69(1986), Nakashio et al. 232(1988), Hirato et al. 248(1990)). It also has poor chemical stability, especially in contact with NaOH in the internal phase (Zhang et al. 73 (1988), Hirato et al. 248(1990)). The chemical instability can be due to hydrolysis of SPAN80 (Van-Peteghem and Abou-Nemeh 186 254(1992) (1990)). They (Hirato et al. 248 (1990)) improved the membrane stability by using Na$_2$CO$_3$ as the internal reagent. It also has solubility in the aqueous phase, which causes a reagent loss.
(Draxler and Marr 1986), Zhang and Xiao 1989, 1990). It could also be destroyed by bacteria (Draxler and Marr 1986) and Ruppert, Draxler and Marr 1988).

The most widely used emulsifier in the LEM studies in literature is SPAN80, which is also called sorbitan- monooleate or sorbitol-monooleate. It has an HLB value of 4.3, which means its oil soluble. It is a nonionic surfactant, and is a mixture of esters of oleic acid and sorbitol. It orients itself at the interface between the droplet and the organic membrane phase, forming a “skin” around the aqueous droplet, such that its hydrophillic end (sorbitan) points towards the aqueous droplet and the hydrophobic end (oleic) towards the membrane phase. SPAN80 has however been found to cause water co-transport and get hydrolyzed. Almost all surfactants conduct water to some extent. SPAN80 (R’COOR), an ester general formula, can hydrolyze in the following way:

\[
R’COOR_{(org)} + H_2O \rightleftharpoons R’OH + RCOOH_{(org)}
\]

**MECHANISM:**

**Acidic Hydrolysis:**

\[
R’COOR \rightleftharpoons R’-OH + R-CO\text{H}_\text{org}
\]
Basic Hydrolysis:

\[
\begin{align*}
\text{O} & \quad \text{slow} \quad \text{O}^- \quad \text{O} \\
\text{OH}^- + \text{C-OR} & \rightleftharpoons \text{HO-C-OR} \rightleftharpoons \text{HO-C} + \text{OR}' \\
\text{R}' & \quad \text{fast} \quad \text{R}' \quad \text{slow} \quad \text{R}' \\
\rightleftharpoons \text{R'COOH} + \text{OR}' & \rightarrow \text{R'COO}^- + \text{ROH}
\end{align*}
\]

ECA4360 is a non-ionic polyamine with a molecular weight of about 1800 (Strzelbicki and Scholosser (1989)) and has a structure (Nakashio et al. (1988)):

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \quad \text{H} \quad \text{O} \\
| & \quad | \quad \| \\
\text{H-C-(C-CH}_2)_n \cdot \text{C-C} & \quad \| \\
| & \quad | \quad \| \\
\text{CH}_3 & \quad \text{CH}_3 \quad \text{H}_2\text{C-C} \\
| & \quad \| \\
& \quad \text{O}
\end{align*}
\]

Where \( n = 10 \) to 60 and \( x = 3 \) to 10. In ECA4360 and its derivatives, polar groups are placed onto a polymeric molecular chain so that the resultant molecule is both a surfactant due to the polar groups and a membrane-strengthening additive due to the polymeric backbone (Li (1981)). ECA 4360 can form very stable emulsions compared to SPAN80 (Goto et al. (1987), Quian, Ma, Shi (1989)). It is sparingly soluble in water (Draxler, Furst and
Marr et al. (1988), Zhang and Xiao (1989, 1990) In addition it can be used at temperatures up to 120 degree centigrade (Li, 1981). This indicates that polyamines are better emulsifiers for ELM than sorbitol esters like SPAN. However, one major drawback of ECA is that it possesses high resistance to interfacial mass transfer, due to the formation of a densely packed, rigid film of polyamine molecules at the membrane interface. In some cases it is known to decompose the extractant in the membrane phase (Draxler and Marr, 1986). A mixture of SPAN80 and polyamine are seen to improve membrane stability and extraction efficiency (Zhang and Wang, 1989).

3.3 - EMULSION PREPARATION

To prepare a stable emulsion, the mean diameter of the dispersed internal phase droplets should be as small as 1 to 3 um, which requires a high input of energy to the water oil system for emulsification. In the laboratory studies, emulsions are usually made by

a. High speed agitators with stirring rates of up to 20,000 rpm. in the laboratories

b. Ultrasonic emulsifiers are also used in the laboratories.

c. For large-scale preparation of emulsions, colloid mills are used to produce very stable emulsions.
3.4 - DISPERSION/ EXTRACTION/ SETTLING

Pretreatment of the feed by filtration is usually required before dispersing the emulsion into the feed. Usually 1 - 10 μm filters are used and sometimes flocculation and sedimentation steps precede the filtration step. During the dispersion operation, agitation in the external continuous phase is done, as a result of which small globules of the emulsion are formed. The globule size is controlled in the range of $1 \times 10^{-4}$ to $2 \times 10^{-3}$ m in diameter. Each globule contains many tiny encapsulated droplets with a typical size of 1 to 3 μm in diameter. These globules containing the encapsulated droplets provide a large interfacial area for both extraction and stripping. After the separation is completed, phase separation of the loaded emulsion from the external raffinate phase takes place in a settler. The settlers are similar to that used for conventional solvent extraction.

3.5 - MODES OF DISPERSION

The dispersion can be carried out either in a batch or continuous mode. Batch operation is normally performed in laboratory work for screening suitable membrane materials, elucidating mass transfer mechanisms, and studying the factors that influence the membrane stability, swelling, and mass transfer rate. The study of the hydrodynamic conditions in a batch process also offers useful information for achieving effective separation. On the basis of batch performance, the optimum membrane formulation and operational conditions can
be determined, and the basic data necessary for the scale up of the separation process can be obtained.

Continuous operation is normally used in pilot plant and industrial processes, and can be carried out with either countercurrent or cocurrent flow. Countercurrent flow is recommended for the contact between the feed and emulsion phase because it can make full use of the internal phase reagent and achieve high extraction efficiency. As with solvent extraction processes, the extraction devices for LEM may be either mixer-settlers or column extractors.

3.6 - EMULSION GLOBULE SIZE

For a given volume of emulsion dispersed in an external phase, the size of emulsion globules determines the mass transfer surface area between the external phase and the emulsion. For a given emulsion volume, the smaller the globule size, more the number of globules, and hence larger the surface area. Globule size of the emulsion depends on the viscosity of the emulsion, the characteristics and concentration of the surfactants in the emulsion, and the intensity and mode of mixing in the dispersion operation. Globule size increases with increasing emulsion viscosity for given mixing conditions i.e., impeller-tip speed of the mixer. High stirring rates decrease globule size but very high stirring speeds can rupture the membrane and cause leakage.
3.7 – DEMULSIFICATION

The breaking of the loaded emulsion is one of the key steps in the liquid membrane extraction process. After liquid membrane extraction, the membrane phase must be recycled repeatedly, and the enriched internal phase is usually recovered.

Two approaches are there for demulsification:

a. Chemical treatment

Chemical treatment involves the addition of a chemical demulsifier to the emulsion. This is very effective but the added demulsifier will change the properties of the membrane phase and it cannot be reused. The recovery of the demulsifier by distillation is also very expensive. Hence chemical treatment is not used for breaking the liquid emulsions. Physical treatment methods include:

a. heating,
b. centrifugation,
c. ultrasonics,
d. solvent dissolution,
e. high shear, and
f. high-voltage electrostatic fields.
Liquid membrane emulsions (O/W and W/O types) can be effectively broken by specially formulated solvent mixture and high shear. The formulated solvent mixture breaks the emulsion without damaging the surfactant. The solvents used are low-boiling compounds, and can be easily recovered later by evaporation. The method of demulsification by high shear requires the use of centrifugation as the first step, followed by pumping the half broken emulsion through a high shear device.

Demulsification by electrostatic fields appears to be the most efficient and economic way for breaking W/O emulsions in LEM processes (Martin and Davis 99(1977), Hsu and Li 256 (1985), Hsu, Li and Huncal 257 (1983, 1983), Draxler, Furst and Marr 68(1988), Feng, Wang and and Zhang 259(1988), Yan and Wang 260(1988), Draxler and Marr 261(1990), Kataoka and Nishiki 85(1990), Van Peteghem and Abou Nemeh191 (1992), Wiencek et al192 (1994)). Electrostatic coalescence is a technique widely used to separate dispersed aqueous droplets from non-conducting oils. This is a physical coalescence and is most suitable for LEM to recover the membrane phase for reuse.