# CHAPTER 7

# Summary and Conclusions

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Emulsion liquid membranes have demonstrated considerable potential as an effective and promising separation technique for a wide range of separations. Factors that favor ELMs over other separation techniques are the inherent simplicity of this technique and the rapidity of separation. Factors that hinder its growth are lack of appropriate and extensive data of various separations and features of emulsion stability and breakage. These aspects need to be continually addressed in order to have a strong case for the adoption of ELM techniques on a commercial scale. This work was primarily taken up to address some of these aspects as detailed in Chapter 1. The significant findings of this work could be classified in three categories related to the following: 1 Characterization of ELMs,
2. Extraction of phenol using ELMs and 3. Extraction of copper and nickel using ELMs

## 7.1 CHARECTERIZATION OF ELMS

The main problems associated with the ELMs stem from the lack of adequate and appropriate information about the W/O emulsions that are used as membranes. It was therefore decided to properly characterize the membranes with respect to physical properties, morphology and dispersion behavior prior to their application for extraction of phenols or metal extractions.

The emulsions were characterized by internal drop size distribution, density, viscosity, and surface tension. W/O emulsions contained NaOH in its inner phase for extraction of phenols, while they contained $H_2SO_4$ for metal extractions. For the case of W/O emulsions containing NaOH solution in the inner phase it was observed that internal drop sizes increased significantly with increase in the volume fraction of the internal phase and also the concentration of NaOH.in the internal phase, while for the case of W/O emulsions containing $H_2SO_4$ in its inner phase, it was found that the internal droplet sizes were very small and the droplets tend to form clusters.

Interesting behavior was observed with respect to viscosity of emulsions containing NaOH in the internal phase. Emulsions were non Newtonian in behavior. The $\eta - \phi$ plots showed a minima at $C_{io}$ value of 0.3 M, uptill a value of $\phi = 0.64$ however such effect was not observed $\phi = 0.69$. It is well known that emulsions tend to form more ordered structures beyond $\phi = 0.64$ hence such behavior could be contributed by the morphological structure of emulsions. The viscosity of W/O emulsions could be predicted with high degree of accuracy using the two-parameter models.

The W/O emulsions with $H_2SO_4$ in the inner phase and carrier in its membrane phase, were considerably more viscous in comparison with the W/O emulsions containing NaOH in the inner phase. Further it was observed that the viscosities passes through a minima with increasing carrier (LIX ) concentration. Two-parameter models could satisfactorily predict the viscosity data for emulsions with $H_2 SO_4$ in the inner phase.

Interfacial tensions showed an increasing trend with an increase in internal phase fraction, increase in the inner phase reagent concentration also increase in the carrier concentration in the membrane. Interfacial tension affects the emulsion globule sizes, hence dispersion behavior of emulsions were considerably affected with increase in interfacial tension that resulted in formation of large size globules. The globule sizes observed for W/O emulsions with NaOH in the inner phase were much larger than that observed for the case of W/O emulsions containing $H_2SO_4$. The Sauter mean diameter evaluated for various dispersions of W/O emulsions containing NaOH could not be predicted satisfactorily using Ohtake correlation (1987). A modified Ohtake correlation is proposed for such cases.

## 7.2 EXTRACTION OF PHENOLS

Various investigators have studied extraction of phenol. However, there is very little work on extraction of other phenols such as o-cresol, p-cresol, 2-chlorophenol etc. Each individual member of this family of phenols behaves uniquely with reference to their extraction characteristics. An objective of this work was to study the batch extraction behavior of the phenols using appropriately characterized membranes. This is necessary in view of the transient nature of the emulsions that leads to experimental data, which does not show reproducibility. In fact one of the main hindrance towards commercialization of ELM technology is the lack of consistency in results obtained. Properly characterized emulsions could certainly help in preparing ELMs with high degree of reproducibility.

The W/O emulsions used in this work were well characterized and displayed a remarkably high degree of reproducibility. Extraction behavior of four phenols namely phenol, o-cresol, p-cresol and 2-chlorophenol were investigated. Effect of numerous emulsion parameters such as: effect of internal volume fraction $\phi$, effect of surfactant concentration $W_{surf}$, effect of internal reagent concentration $C_{io}$, in addition to the effect of operating parameters such as the Treat ratio, stirring speed and initial feed concentration was investigated. These investigations are reported in Chapter 4. Critical analysis of the experimental data revealed that the molar ratio M of the inner phase to the external phase is the dominant parameter effecting extraction. The molar ratio is a measure of the capacity of the emulsion to extract the solute. It was found that very rarely NaOH utilization was more than 50 %.

In addition to the above effect of membrane material was also investigated. Results indicate that kerosene is perhaps the best membrane material that can be used to prepare ELMs. Further the effect of surfactant type, degree of swelling also aspects of membrane breakage were investigated for all the solutes. It was observed that the NaOH concentration in the inner phase is the key factor that affects membrane stability. Valuable data in this direction was obtained that can be conveniently used to model emulsion breakage in future.

Extraction of solutes such as phenols etc using NaOH in the inner phase are typical representative of Type I transport mechanism. This mechanism involves maximization of the driving force within the emulsion globules by having a chemical reaction within the emulsion globules between the solute and internal reagent. Type I transport could be conveniently modeled using the Advancing front model of Ho *et al.* (1982). This model was used to simulate the extraction behavior of the phenols as reported in Chapter 6 based on experimentally determined parameters. It was found that the advancing front model could predict the extraction behavior quite well for high solute concentrations but failed to predict the extraction behavior of solutes when present in relatively low concentrations.

Such behavior stems from the conjuncture that the reaction between phenols and NaOH are irreversible. Bunge and Noble (1984) proposed a reversible reaction model that could account for such discrepancy. The reversible reaction model was also simulated for extraction of phenols and a reasonably good fit was observed between the experimental and predicted values for extraction of phenols with low solute concentrations as can be seen in Chapter 6.

## 7.3 EXTRACTION OF COPPER AND NICKEL

The solvent recovery of copper from acid leach liquors is extensively practiced in the hydrometallurgy industry. Copper recovery from feed at low concentrations is not feasible using solvent extraction due to severe reagent losses. Thus, ELMs have strong potential for being utilized in copper recovery. Although there exists some data on copper recovery using ELMs but most of it is dated since the carriers used in those investigations are commercially phased out.

The extraction of copper using ELMs was investigated in this work. Three commercially used extractants namely LIX 84, LIX 84 I and LIX 984 NC were studied. These extractants are chelating type and belong to the family of hydroximes. LIX 84 and LIX 84 I are moderately strong extractants while LIX 984 NC is a very strong copper extractant. Copper extraction with ELMs containing LIX 84 I or LIX 984 NC in the membrane phase has not been reported in literature.

Copper extraction from sulfate solutions using ELMs containing LIX 84 also LIX 984 were conducted with well characterized W/O emulsions. The effect of various parameters such as pH, $\phi$, $C_{io}$, $C_C$, $W_{surf}$, Treat ratio also the stirring speed on the extraction of copper was studied. It was found that pH is the dominant parameter. Based on the extraction behavior at pH of 2 and 5 it could be concluded that the LIX 984 NC was a far superior extractant in comparison with the widely used LIX 84 extractant.

LIX 84 I is a ketoxime while LIX 84 is a mixture of 90% ketoxime and 10 % salicylaldoxime, LIX 984 NC is a mixture of 50 % ketoxime and 50 % salicylaldoxime. Salicylaldoximes are very strong copper extractant but they don't get stripped easily hence blending with a ketoxime helps in improving overall properties

There is considerable interest in extraction of copper at low pH (less than 2). It was observed that LIX 984 NC works admirably even at pH = 1 while LIX 84 was not able to extract the solute substantially under those conditions. Other than chelating reagents even the thio analogs of organophosphinic acids are known to extract copper in preference to other metals. One such commercial reagent namely CYANEX 302 was also used as a carrier for copper extraction at pH =2 it gave a performance comparable to LIX 984 NC.

Copper extraction from ammoniacal media is also an area that has considerable potential for particularly directed towards the recovery of copper from scrap metal literature suggests that LIX 84 I could be conveniently used for extraction of copper from ammoniacal media. This, extraction was explored using ELMs and quantitative removal of copper was obtained at 8.1 pH in just 3 minutes. However, the associated problems of membrane instability require to be addressed since severe breakage is encountered in ammoniacal media.

Nickel extraction using chelating reagents is practiced in the industry. The possibility of using ELMs was explored for nickel extraction from ammoniacal as well as sulfate media. It was observed that nickel gets loaded in the membrane phase but just does not get stripped using either sulfuric acid or ammonia inside the reagent phase. Hence, quantitative removal was not obtained. Combined extraction of copper and nickel yielded separation factor of 100 that can be further improved upon by selection of proper operating conditions.

## 7.4 SCOPE FOR FUTURE WORK

Emulsion liquid membrane separation is still in its nascent stage of development it offers considerable potential for exploitation in various applications. The success of ELM technique largely depends on the stability and consistency of the membranes hence, it is necessary to aggressively pursue research to develop more stable W/O emulsions. The surfactant is often the key hence more emphasis requires to be put on developing appropriate surfactants for these applications.

There is lack of data on the continuous extraction of solutes using ELMs hence that area requires focus. Demulsification behavior of ELMs has been very scarcely touched upon it is an area which is of critical importance in the commercial application of this field hence research in the area of demulsification will be of great interest in this field.

Separation of metals at low pH and from mixtures is another area of ELMs that will hold attention of researchers in coming years. There is a lot of work that needs to be done in almost all aspects of emulsion liquid membrane separations, it is felt that in future there will be hectic activity in this area.