New Vistas in Liquid Emulsion Membrane Technology

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Introduction

Liquid Emulsion Membranes (LEMs), first discovered by Norman Li in 1968, are three phase systems consisting of double emulsions which offer the singular advantage of extraction between two completely miscible phases. They are also known as liquid surfactant membranes.

One of the two miscible phases is encapsulated in the form of droplets in an immiscible phase (forming an emulsion stabilized by surfactants) and this emulsion is, in turn, dispersed in the form of globules in the second miscible phase. The immiscible phase thus acts as a liquid membrane preventing contact between the interior and exterior phases (Fig. 1). The globules are non-coalescing and retain their integrity throughout the process. The presence of surfactants prevents the circulation of internal phase droplets inside the globule.

LEMs may either be water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) systems, the former being more commonly employed.

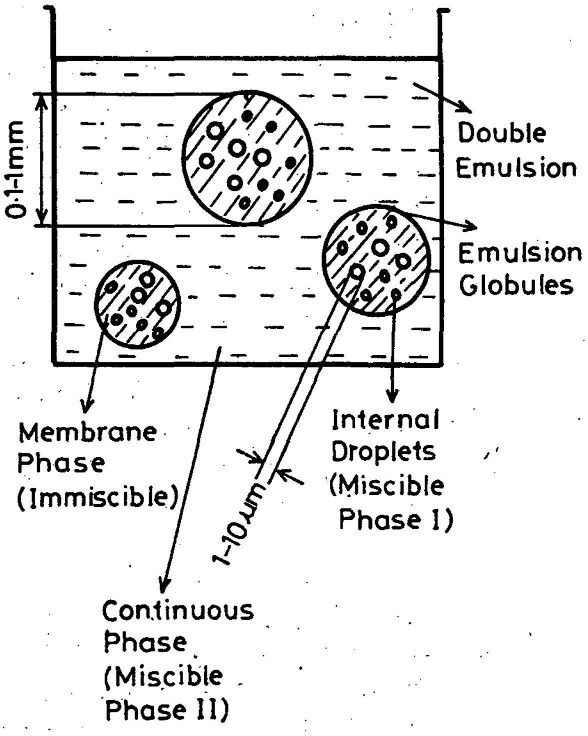

Fig.1. Liquid Emulsion Membranes (LEM)

Mechanisms Of Transport

There are two principal mechanisms by which transport of materials occurs across LEMs:

1. **Simple transport** : When a substance is directly soluble in the membrane phase, transport occurs by simple permeation, due to the concentration difference across the membrane. However, the process progressively slows down and finally ceases when the concentrations in both the internal and external phases are identical.

2. **Facilitated transport:Type I facilitation** (Fig. 2) In order to avoid the decrease in the driving force with increasing concentration in the internal phase, the transport is facilitated by converting the permeated component to a form that is insoluble in the membrane phase thus preventing backtransport. This is achieved by the use of a suitable encapsulated reagent which usually is an acid or a base. For instance, NH_3 may be converted to NH_4^+ and the concentration gradient maintained.

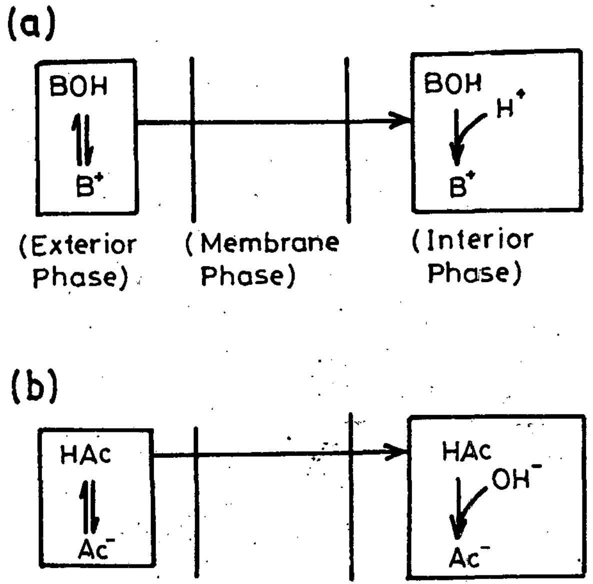

Fig.2. Type I facilitation

(a) Extraction of a base (NH$_3$)

(b) Extraction of an acid (Phenols and carboxylic acids)

Type II facilitation: (Fig. 3) In this case, the permeate is usually an ionic species and therefore insoluble in the organic membrane phase. Hence, a mobile carrier principle is adopted. The carrier, a complexing agent, forms a soluble complex with the ionic solute and this complex is then transferred across the membrane phase. The complex formation and dissociation may be driven by ion pumping which may be:

(a) Co-transport: Diffusion of oppositely charged ions in the same direction.

(b) Counter transport: Diffusion of like charged ions in the opposite direction.

For example, in the extraction of metal ions, proton may be used as the counterion by having a high concentration of acid in the interior phase. The resultant reactions in combination with the backtransport of the complexing agent (thus achieving extraction and stripping in a single step) can force a material transport of a component against its own concentration gradient.

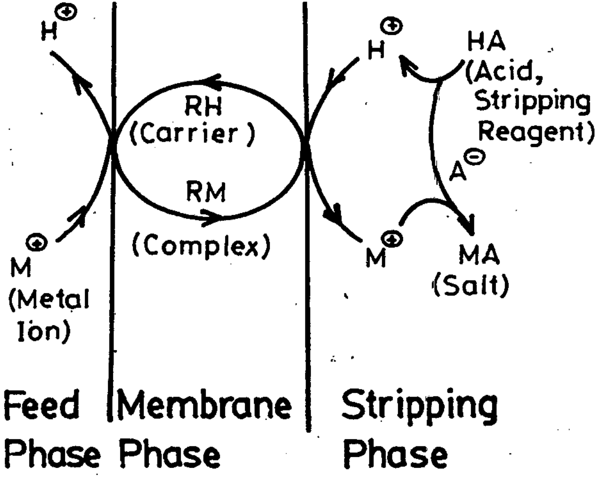

Fig.3. Type II facilitation
(for a metal ion extraction)

In both of these transport mechanisms, facilitation helps to overcome equilibrium limitations and effects the transport of the component to a small, manageable volume.

Operation Of A Commercial LEM System

The Following properties of LEMs are exploited for commercial applications :

1. Ability to act as a very selective transfer agent (on account of the carrier).

2. Capacity to offer an increased contact area for mass transfer owing to the small size of the interior droplets (of the order of μm).

3. Stability over a long period.

4. Susceptibility under appropriate conditions.

A commercial LEM extraction system (Fig. 4) uses the following steps :

The first step is the emulsion formation between phases I and II. Phase I contains the stripping solution consisting of dilute acids and bases, while phase II is the inert membrane phase (kerosene or paraffin oil) with surfactants and carrier additives. This W/O (or O/W) emulsion is prepared in a conventional mechanically agitated contactor.

Next, we have the mixing of the above emulsion and phase III. Phase III is the feed phase itself containing solutes to be extracted. A stirred contactor in the form of a continuous countercurrent column or a batch mixer may be used for contacting the phases. This results in phase I of the W/O emulsion getting enriched with the solute.

After the extraction process, the

separation of the W/o emulsion from the double emulsion is carried out is a settler by way of gravity, temperature, alternating electric field, electrolytees, ultrasound or centrifugal force.

Finally, we have the breakup of the W/O emulsion. This is performed in an electrostatic coaleser. The solute is thus recovered from Phase I and Phase II is recycled for reuse.

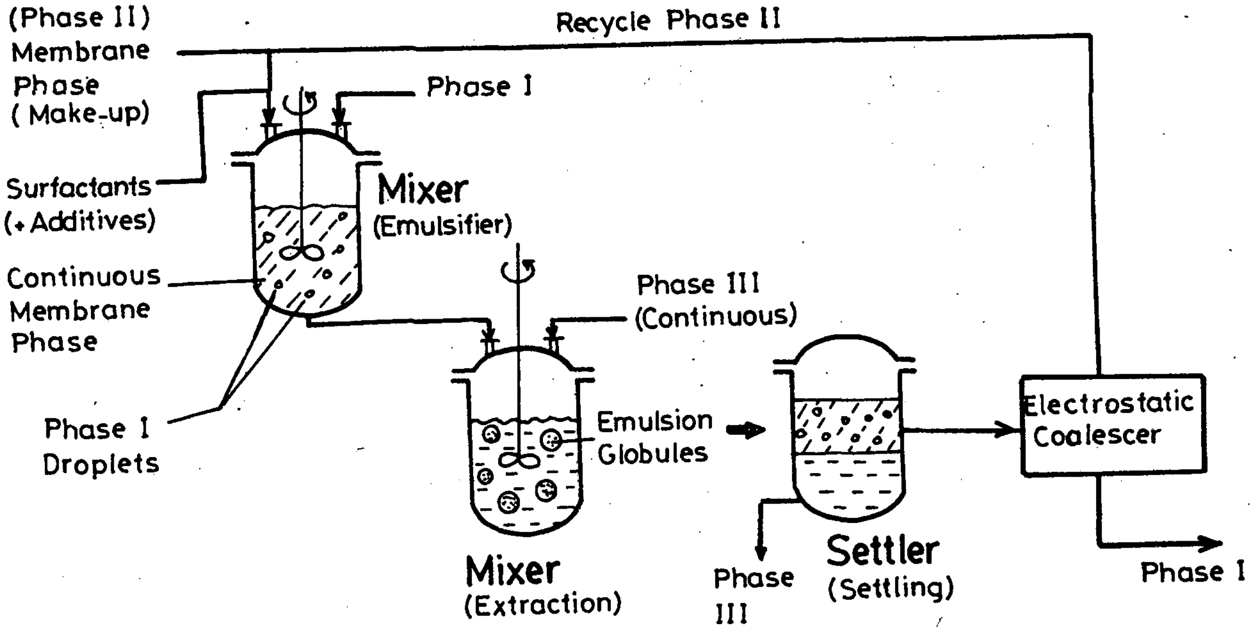

Fig. 4 . Operation of a commercial LEM system

Drawbacks Of Conventional LEM Technology

1. On prolonged contact of the gloubles with the feed stream in the stirred contactor, the emulsion swells with water, increasing the internal phase volume. The aqueous content of the emulsion increases from 10 - 20% at the start to up to 35 - 50% at the end of the process. This swelling, which occurs due to osmotic gradients, in addition to reducing the stripping efficiency and diluting the driving force, also leads to an increase in the viscosity of the spent emulsion making it more difficult to emulsify.

2. The conventional LEM systems employed use surfactants to lower the interfacial tension and stabilize the emulsion globules. This necessitates the use of separate emulsification, extraction, settling and demulsification units. The overall cost of the process can be markedly reduced if one or more of these stages are eliminated.

3. Another disadvantage is that the high shear induced by the impeller rotation at increased speeds results in membrane breakage leading to leakage and backmixing. On the other hand, lower shear rates will result in mass transfer resistances becoming dominant. It is desirable, therefore, to have a dispersion free process.

4. The reagent encapsulated in the internal droplets is generally consumed in the process and this extracted material is discarded which is not desirable due to the high cost of chemicals.

Recent Developments

Some recent developments, which circumvent the above limitations, are categorised below:

Microporous Hollow Fibre Contacting (HFC)

HFC is emerging as an alternative method to the direct dispersion of emulsion liquid membranes. It is more akin to a supported liquid membrane process. This method of contact retains the essential advantage that LEMs separations offer, i.e., extraction and stripping in a single step (thereby avoiding equilibrium limitations).

Hollow fibre contactors consist of microporous hydrophilic or hydrophobic fibres (depending on whether it is a W/O/W or an O/W/O system) arranged in a shell and tube configuration as shown in Fig. 5.

The wetting membrane phase (organic for a W/O/W system) containing the strip droplets is present in the lumen of the hydrophobic fibres with the aqueous phase on the shell side. The wetting phase preferentially fills the pores and is thus in direct contact with the aqueous phase. By maintaining a higher pressure on the shell side, the interface between the membrane and the outer aqueous phase is immobilized at the pore entrances on the aqueous side. This pressure should be less than the breakthrough value (at which the aqueous phase will penetrate the pores).

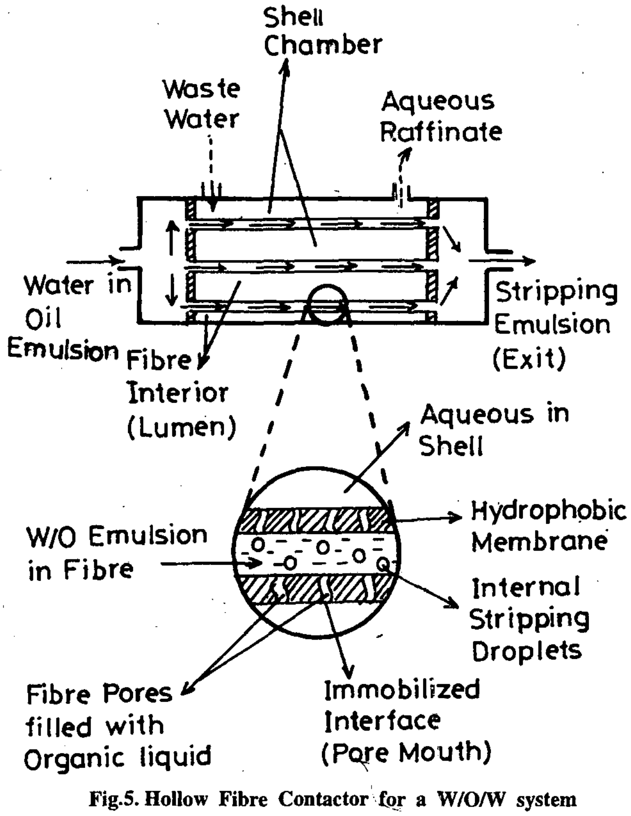

Fig.5. Hollow Fibre Contactor for a W/O/W system

The steps involved in hollow fibre extraction can be summarised as below:

1. The solute, as it passes from the shell side into the emulsion contained in the fibres, initially overcomes the resistance to mass transfer in the external aqueous phase.
2. The second step is the reaction at the pore interface between the carrier (in the membrane phase) and the solute (in the external aqueous phase) to form a soluble complex.
3. The complex then diffuses through the hollow fibre pores to the interior of the fibre.
4. Finally, there is the migration of the complex to the stripping phase droplet in the emulsion and interfacial reaction between the membrane phase and the stripping phase. The solute is thus transferred to the stripping phase and the carrier regenerated.

Emulsion extraction of Cu has been studied using LEMs by Raghuraman et al, in both a hollow fibre (HFC) and a stirred contactor (SC) as shown in Fig. 6. It is observed that while SC extraction is only upto 1 ppm, HFC results in the Cu concentration going down to as low as 20 ppb. The higher rate of extraction in case of SC is due to the larger interfacial area, but the leakage of the internal phase contents results in a lesser extent of extraction. The leakage is upto 40% for SC and close to none in the case of HFC. Water in the emulsion phase in the SC swells from 13 to 16.5%, while effectively no swell is observed in the case of HFC.

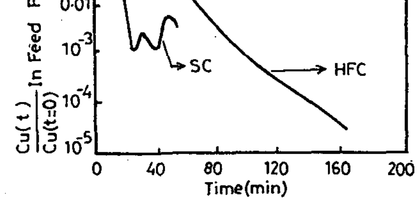

Fig.6. Comparison of Cu extraction using SC & HFC

Table 1: Operating parameters

Extracting agent	5%(wt) LIX
Treat ratio	10 :1
pH of aqueous feed phase	5.36
Internal stripping phase%(wt)	18
SC :	
Stirrer rpm	400
Aqueous phase volume	300 cc
LEM volume	30 cc
HFC: Aqueous shell flow rate	40 cc/min
Aqueous phase volume	270 cc
LEM volume	27 cc

The following advantages make HFC a viable proposition:

1. The hollow fibres owing to their high packing density (by design) have a large surface area to volume ratio, thus increasing the available area for mass transfer.
2. It being a dispersion free process, shear rates are much lower and this results in improved efficiency of extraction with reduced membrane swelling and breakage.
3. Besides being non-wetting, the internal phase droplets are of the order of 1-10 microns, while the pores in the hollow fibre contactor are of the order of only 0.05 microns. This disparity in size effectively eliminates the possibility of these droplets being contained in the pores. This prevents direct contact between the miscible phases and thus, not only avoids the use of the settler at the end of the extraction but in addition, minimizes leakage and swell.
4. The stability of the emulsion in this case is maintained by the turbulence as it flows through the fibres and hence, one can afford to employ less stable emulsions. This reduces the expense of demulsifications. In fact, it is possible to extend this advantage all the way upto zero surfactant concentration where the emulsion would be nothing but an oil-strip phase mixture free of surfactant.

The extraction of Cu from an aqueous feed in a HFC using an emulsion and an oil-strip phase mixture has been studied by Raghuraman et al. and the results are found to be comparable as shown in Fig. 7.

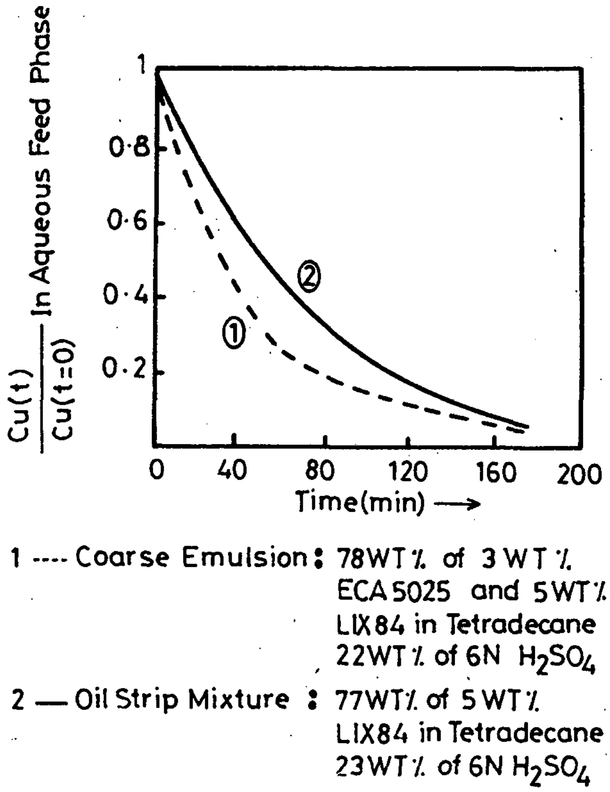

Fig.7. Comparison of results of Cu extraction using
(i) Coarse emulsion
(ii) Oil-Strip mixture

Table 2: Operating Parameters

Shell	Aqueous feed phase	
	pH	1.6
	Flow rate	62.8 cc/min
	Volume	317.6 cc
Tubes	Emulsion or oil-strip mixture Flow rate	117 cc/min
	Volume	250 cc
Configuration	Total recycle of both phases	

Hence, as emulsion stability is not a criteria in HFC, it also avoids the problem involved in the selection of the surfactant, which is often specific to a particular system. The LEM system incorporating an HFC is as shown in Fig. 8

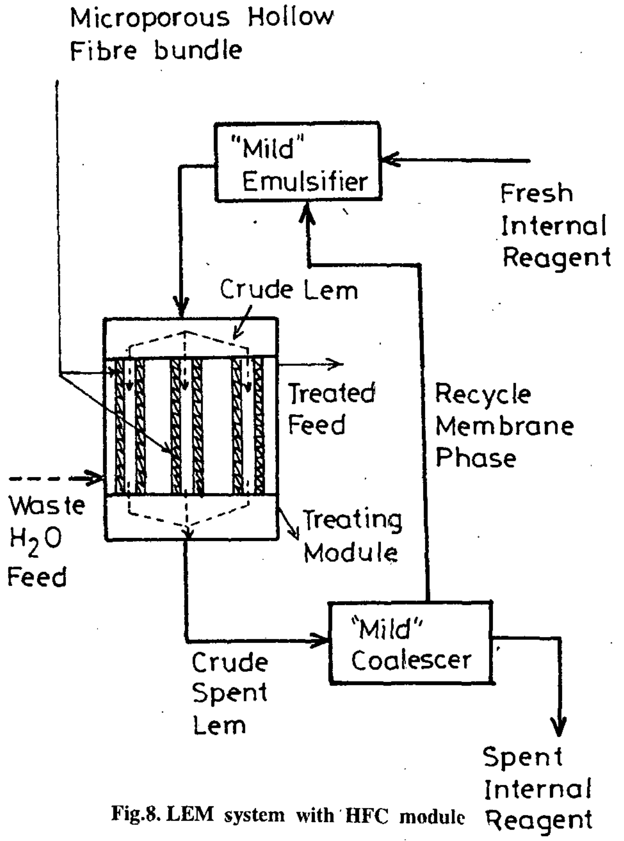

Fig.8. LEM system with HFC module

Electrostatic Pseudo Liquid Membranes (ESPLIM)

Boyadzhiev and Kyuchoukov had originally developed the two-cell technique which avoids the use of a surfactant. A modified form of this concept, a combination of solvent extraction, liquid membranes and electrostatic techniques has led to the development of the highly efficient process of ESPLIM.

Under a sufficiently high electric field (above critical feed strength), a water drop inside a continuous phase will burst into numerous droplets. This is called electrostatic agitation.

As shown in Fig. 9, there is a Reaction Tank filled with an organic solution containing extractant. Its upper part has a baffle plate which divides it into an Extraction cell and a Stripping cell. The lower part incorporates a blank plate dividing it into an Extraction settler and a Stripping settler. The aqueous solutions in the form of droplets in the respective cells remain separated, but the organic solution mixes freely via the baffle plate.

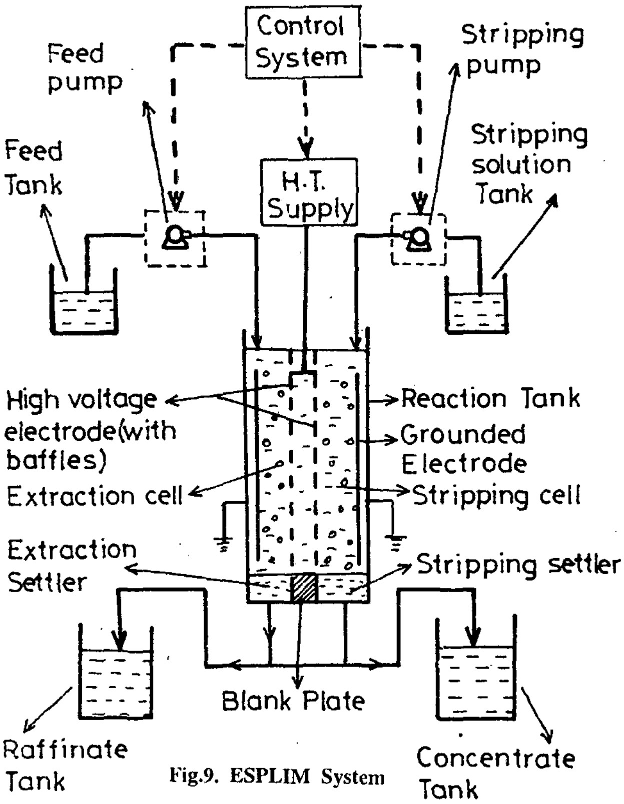

Fig.9. ESPLIM System

The integrated baffle electrode consists of inclined baffles made of plastic which separate the feed and the stripping solution and prevent the droplets from intermixing (Fig. 10).

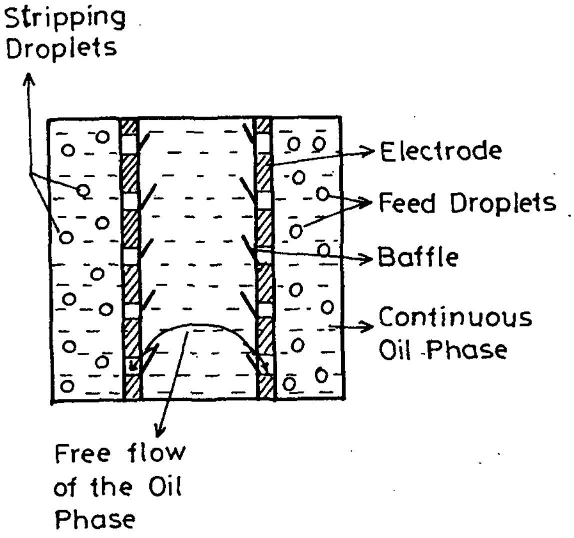

Fig.10. Structure of Baffle electrode

The sequence of operations is as given below:

i) A high voltage electrostatic field is applied across the extraction and stripping cells simultaneously by way of the inserted electrodes. The feed solution and the stripping agent are then fed to the extraction and stripping cells, respectively, wherein they get dispersed by electrostatic agitation.

ii) In the extraction cell, the solute in the aqueous feed is extracted by the carrier into the continuous oil phase. The resultant complex (in the oil phase), on account of its own concentration gradient, diffuses through the baffle plate into the stripping cell..

iii) The complex now interacts with the stripping aqueous droplets and in the process, the extractant is regenerated which diffuses back to the extraction cell.

iv) While these interactions occur, the aqueous droplets, under gravity, continuously move downwards in the oil phase thereby enabling counter current extraction and stripping in the two cells.

v) The aqueous raffinate and concentrate are collected in the respective settlers.

The results for Cobalt ion extraction (Co^{2+}) extraction are as given in Table 3.(Gu, Z.M., 1990).

Table 3: Operating Parameters for Co^{2+} extraction

Process conditions :		
Feed solution	:	1000ppm Co^{2+} 0.1M NaAc
Stripping solution	:	1.0 M H_2SO_4
Oil phase	:	10% D2EHPA in kerosene(v/v)
Operating Conditions:		
Voltage	:	3.0 kV
Feed flow	:	200 ml/hr
Current	:	650 μm
Flow rate of reagent	:	10 ml/hr
Mean residence time of droplets	:	4 sec
Results:		
Co^{2+} concn. in raffinate	:	10 ppm
Co^{2+} concn. in concentrate	:	19750 ppm
Extraction efficiency	:	99%

ESPLIMs present the following benefits:

1. All the advantages of LEMs are retained such as reduced number of stages and solvent consumption.

   ESPLIMs are characterised by a lower consumption of internal reagent.
2. Much higher treat ratios of upto 50: 1 can be employed as compared to other LEM systems.
3. In ESPLIM, the electrostatic field stabilises the dispersion by the lowering of interfacial tension. This is by the generation of a mechanical force on the surface of the water droplets, acting outward and therefore in a direction opposite to the surface tension which lowers the system surface energy. This thus effects saving in the surfactant and the demulsification operation.
4. As compared to conventional mechanically agitated units,
   a) There are no moving parts which makes this system especially useful for radioactive effluents.
   b) Lower energy consumption
   c) Greater mass transfer
5. The transport in this case is by convection of droplets. Hence, there is no diffusional resistance. The flux is, in addition, enhanced by the Marangoni's instability arising out of variation in the interfacial charge density between the aqueous droplets and the oil phase (caused by the applied field) and leading to interfacial turbulence.

6. The use of a baffle plate eliminates the instability and fouling problems commonly associated with membranes.

However, the continuous solvent phase employed in this system should necessarily be non-polar and hence this method of extraction is applicable only to W/O/W systems. The ESPLIM technology is in its incipient stages. There is a need to study its performance for various systems (other than Co) which are normally encountered in industrial effluents. Efforts are on to enhance the efficacy of ESPLIMs and these include improvements in the system setup, particularly the structure and materials of the components like the baffle electrode. These developments may see ESPLIMs emerging as a future competitor in the field of waste-water treatment.

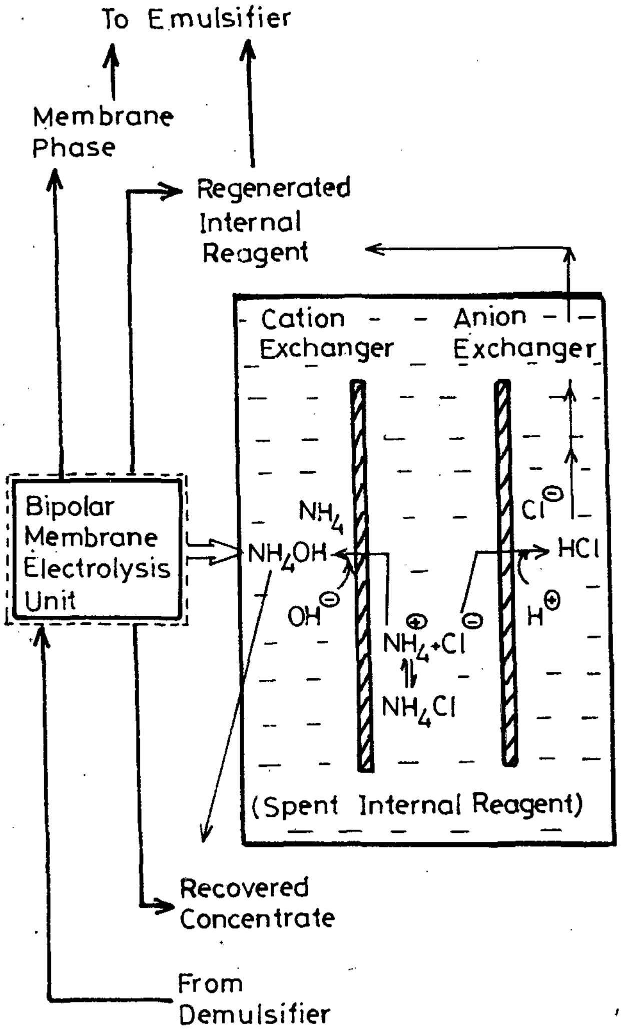

Fig. 11. LEM system coupled with a Bipolar Membrane unit (for NH_3 extraction)

Combined Liquid and Bipolar Membrane unit

The chemical consumption in an LEM process can be improved significantly when the internal reagent is an acid or a base so that the driving force is neutralization. In such a case, the spent internal reagent in its salt form can be subjected to a Bipolar membrane process which effectively regenerates fresh reagent and liberates the permeate in a recoverable unneutralized form. The general layout of such a process is as given in Fig. 11.

Conclusion

As is evident in the above discussion, innovations like the microporous hollow fibres, electrostatic pseudo LMs and the coupled LM-Bipolar membrane units make the already established LEM technology all the more attractive. These modifications, having enabled one to circumvent the use of settling and demulsification units, possess the potential of significantly bringing down the cost of the LEM extraction system. The judicious exploitation of these techniques will probably see commercial applications extending beyond the present areas of wastewater treatment and hydrometallurgy.

References

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