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A. M. Sastre[a]; A. Kumar[a]; J. P. Shukla[b]; R. K. Singh[c]
[a] Departament d'Enginyeria Química E.T.S.E.I.B., Universitat Politènica de Catalunya, Barcelona, Spain
[b] Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India [c] PREFRE Plant, Fuel Reprocessing and Nuclear Waste Management Group, Bhabha Atomic Research Centre, Tarapur, India

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IMPROVED TECHNIQUES IN LIQUID MEMBRANE SEPARATIONS: AN OVERVIEW

A.M. SASTRE[a,**], A. KUMAR[a,*], J.P. SHUKLA[c] AND R.K.SINGH[b]

a, Universitat Politècnica de Catalunya, Departament d'Enginyeria Química
E.T.S.E.I.B., Diagonal 647, E 8028 Barcelona, Spain
b, PREFRE Plant, Fuel Reprocessing and Nuclear Waste
Management Group, Bhabha Atomic Research Centre,
Tarapur, 401502, India
c, Radiochemistry Division, Bhabha Atomic Research Centre,
Trombay, Mumbai-400085,India

ABSTRACT

This paper presents a brief overview of improved Liquid membrane (LM) separation techniques, including modified bulk, supported and emulsion liquid membranes as well as hollow fibre contained liquid membranes, electrostatic pseudo liquid membranes (ESPLIM) reverse micelle and recently developed hybrid (HLM) and other LM configurations. The discussion also includes design of ion specific carriers, analytical importance, aspects of stability and modelling of LMs and their applications in the separation/removal of metal cations from a range of diverse matrices. In general, an attempt has been made to review the literature published from 1990 to 1997 in order to focus on the present status of different liquid membrane configurations. The LM studies dealing with separation and removal of organic compounds and gases are not included in this article owing to limitations of space.

Keywords: Liquid membranes; Bulk liquid membrane; Electrostatic pseudo liquid membrane; Hybrid liquid membrane; Hollow fibre contained liquid membrane; Polymer inclusion membrane; Reverse micelle; Supported liquid membrane

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[*] On leave from: PREFRE, Bhabha Atomic Research Centre, Tarapur, INDIA
[**] Corresponding author
Fax: (3493) 4016600; Email: sastre@eq.upc.es

The review is structured into the following sections:

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Bulk liquid membrane
Supported liquid membrane
Polymer inclusion liquid membranes
Emulsion liquid membrane
Electrostatic pseudo liquid membrane
Reverse micelle
Hybrid techniques
Modelling of different LM processes
Summary

INTRODUCTION

As reflected by the large number of contributions to the scientific literature over the past decade, the impetus is on the development of new chemical separation techniques, particularly for liquid wastes and effluents. This situation was brought about not only by increasing concern about environmental problems, energy savings and optimisation of a wide range of industrial processes but also by recent findings in the field of fundamental chemistry and the analytical importance of the new techniques.

Diffusion-limited transport of molecules and ions across liquid membranes (LMs) represents a powerful new tool which excels most conventional separation techniques since it combines extraction, scrubbing and regeneration into a single step. The separation and concentration of materials constitutes a very important operation and it has a long history of improvement and diversity. Membranes for separation and concentration possess such characteristics as expediency of operation, energy related advantages, lack of side reactions, a high functional capacity etc., and have applications in a wide variety of fields (1). LMs are expected to play a leading role in science and technology in the near future, and continuous efforts are being made to develop improved functions in these membranes (2-7).

The separation of metals by LMs was actively investigated for its application in hydrometallurgy by Li et al. (7a). In 1986, a process to recover zinc from waste streams at a textile plant in

Austria was developed as the first liquid membrane process on a commercial scale by Marr et al. (7b). It is interesting to note that future trends of LM techniques are quite encouraging; they continue to command significant attention, as indicated by the large number of papers published between 1990 and 1997 (based on Current Content Search ®) (Fig. 1).

The importance of LMs is unquestioned, particularly in instances where solute concentrations are extremely low and large volumes of solutions must be processed without generating any secondary wastes. LM techniques have been extensively deployed in separation science for such processes as metal recovery from leaching and waste waters, extracting precious (8a) and strategic metals from natural waters, and treatment of large volumes of the toxic and hazardous effluents generated by nuclear and allied industries (8b). Increasing numbers of commercial operations unequivocally demonstrate imaginative applications of membranes in myriad fields. LM technology as applied to waste treatment/reduction and environmental monitoring problems offers several advantages over classical management options. Though the pertraction has yet to attract large scale industrial applications, several operational pilot plants successfully testify to its potential.

In an LM system where the distribution of permeant solute between the feed phase and the LM phase is higher than that between the receiving phase and the membrane phase, uphill transport of solute is possible. However, double-phase liquid-liquid extraction is an equilibrium limited process whereas LM permeation is commonly regarded as a non equilibrium steady state process or rate controlled process with several rate processes in series.

Recently, liquid membrane processes have been proposed as a clean technology owing to characteristics such as their high specificity, intensity and productivity as well as low emissions and energy utilisation. Each characteristic has been described by Pickering et al. (9) in order to justify their effectiveness as clean technology. With the objective of "clean technology" in mind, liquid membranes are continuously modified in efforts to attain improved performance in terms of stability and efficient metal transport. In the initial period of development, these LM techniques were reported for industrial applications in cleaning waste water by emulsion formation (7). Subsequently, the modified configuration of bulk liquid membranes with the concept of pertraction was used by Boyadzhiev (10) for the removal of Cu(II) and Zn(II). Recent studies performed by Kralj and co-workers (11) indicate the potential of LM applications such as selective dissolution of copper oxalate from a suspension of copper, calcium and cadmium oxalate using LIX 84/kerosene and Durapore as a support across a flat sheet supported liquid membrane (FSSLM). With a view to overcoming the stability problems of hollow fibre supported liquid membranes, Sirkar et al. have carried out extremely useful research activity on hollow fibre contained liquid membranes (HFCLMs). They have successfully demonstrated

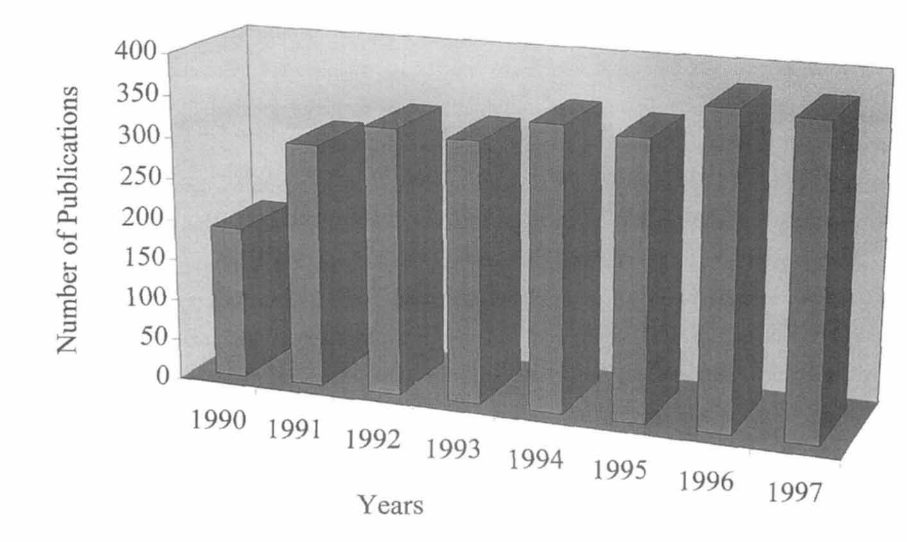

Fig. 1. Number of publications which appeared in various journals pertaining to liquid membranes during the period 1990-1997.

HFCLMs for efficient metal transport with better stability and reproducibility for the various chemical separation schemes (12-15). Recently, another example of LM configuration, namely hybrid liquid membranes (HLMs), was reported as a newer technique which is also claimed to be quite stable for continuous membrane impregnation (16-17). Schlosser and Rothova recently published results of a new type of hollow fibre pertractor, in effect a flowing liquid membrane, which was reported to be similar to HFCLMs (18). Further, to eliminate the emulsification and de-emulsification problems of emulsion liquid membranes (ELMs), a relatively new variation of liquid membranes, the so-called electrostatic pseudo liquid membrane (ESPLIM), was developed in China by Gu et al. (19). The technique was claimed to be more stable than supported liquid membranes. Reverse micelle (RM) or Microemulsion, which is similar to the LM system, has also attracted much attention as a new separation technique, although few applications for metal separation have been reported (20). In order to improve the stability and selectivity of a liquid membrane, Bartsch et al. (21) proposed a new method for obtaining synthetic polymeric ionomer membranes for use in metal separation. They have carried out a chemical modification of perfluorinated ionomer membrane material by binding monoazacrown ether in the membrane for alkali metal cation transport.

It is expected that, for membrane processes being introduced on a continuous impregnation basis, both HFCLMs and HFSLMs will have potential for future separation schemes. In

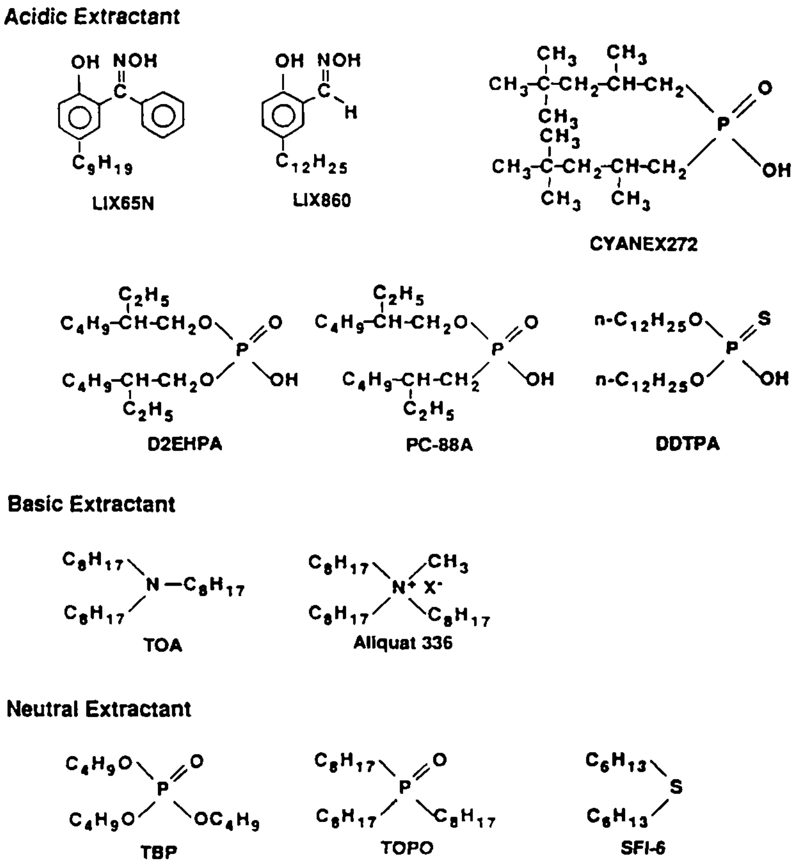

Fig. 2. The chemical structures of commercial extractants used in different configurations of LMs (reproduced with the permission of the Society of Chemical Engineers, Japan, Ref. 104).

addition, their applications for determining the trace level concentration of metal ions are of paramount importance owing to their high selectivity and ability to concentrate the aqueous streams. Recently, a number of studies on SLMs and HFSLMs have been reported which are related to the analytical importance of the technique used for the determination of precious and heavy metals (22-26).

The commonly used carriers in different configurations of liquid membrane studies and some of the recently employed new surfactants are shown in Fig. 2 and Fig. 3 respectively.

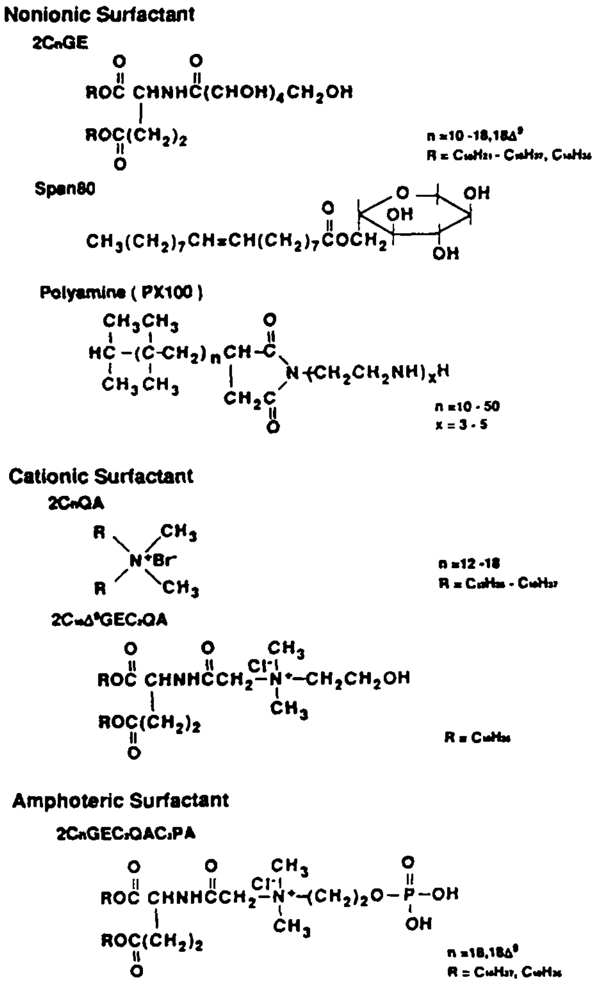

Fig. 3. Recently developed surfactants for use in ELM studies (reproduced with the permission of the Society of Chemical Engineers, Japan, Ref. 104).

In this paper, we present a brief overview of improved techniques in liquid membrane (LM) separations, including modified bulk, supported and emulsion liquid membranes as well as HFCLMs, ESPLIMs, RMs and the recently developed HLMs. The discussion also includes applications of such LMs in the separation/removal of metal cations from a range of diverse matrices. The design of ion selective carriers for LM studies, their analytical importance and modelling of various LM processes are also presented. The LM studies dealing with separation and removal of organic compounds and gases are not included in this article owing to limitations of space.

Before an in-depth consideration of advances in LM techniques, one should be familiar with the fundamentals of cation transport, which is more or less similar in all types of LM techniques.

Facilitated and coupled transport

The use of a liquid phase can enhance the solute flux owing to the higher diffusion coefficients in liquids than in solids. The addition of non-volatile complexing agent to a liquid membrane enhances permeability of solute by several orders of magnitude (27-28). This organic carrier molecule can react selectively and reversibly with the solute. The selectivity and flux of metal ions are improved by this reversible reaction of the carrier and the solute.

Facilitated transport is concerned with the reversible reaction between the solute and the carrier. It is not coupled to other components. This reaction normally takes place throughout the liquid membrane phase. Similarly, in the concept of coupled transport the reversible reaction takes place as an ion-exchange reaction, and the solute flux is linked (coupled) to the flux of another ion (29). The carrier (acidic extractant) is a cation exchanger reagent. The ion-exchange reaction normally occurs at a liquid-liquid interface since metal ions are not soluble in the organic membrane phase. Coupled transport is analogous to performing solvent extraction in a thin film. The majority of liquid membranes for metal ion separation involve a coupled transport mechanism.

IMPROVED TECHNIQUES IN LIQUID MEMBRANE SEPARATION

A brief description of improved techniques in LM separation and their applications for metal separations and recent advances is given below.

Bulk liquid membranes (BLMs)

In BLMs, two miscible aqueous liquids (feed and strip) are separated via a third immiscible organic liquid (carrier). The mass transfer from one liquid (feed) to the other liquid (strip) takes place via the carrier. Because transport through the bulk takes place by convection, the unstirred boundary layer often forms the largest transport resistance. BLMs are frequently used to investigate novel carriers, carrier systems or transport mechanisms. Their main function is to optimise data for both SLMs and ELMs. The principal disadvantage of traditional BLMs has been the low interfacial surface areas and mass transfer rates as compared to SLMs and ELMs. Direct scale-up of this type of contactor is therefore very impractical.

Recently, BLMs with improved mass transfer design have been presented in which mass transfer rates could be enhanced (30). The use of a hollow fibre contactor between the phases provided a far higher interfacial area than that which normally exists (31). The other design again uses a porous hydrophobic membrane phase, which provides the means of partitioning the dispersed source and continuous receiving phase. This design is similar to that of SLMs (32), although the continuous organic phase was deliberately added to the dispersed aqueous phase. Owing to the local pressure difference across the membrane, the organic solution moved through the pores of the membrane. The solute dissolved into the membrane solution, and then is transferred across the pores membrane with the bulk motion of the membrane solution; i.e. the organic phase acts as a bulk liquid membrane. The movement of a membrane solution across the porous membrane could enhance the mass transfer rate, which enables rapid separation of the solute. The additional advantage of this system is better stability, although more pumping and settling units are required.

Hayashita (33) performed the studies with BLMs, where separation of the source and receiving phases is provided by an organic solution, anion-exchange membrane or plasticised membrane. To improve upon the stability aspects of liquid membranes, Hayashita and others (34) developed the polymeric membrane separation, which affords metal separation ability comparable to that of the liquid membrane. They designed a dialysis cell utilised for the bulk liquid membrane separation. The source, membrane, and receiving phases were separated from each other by cellulose dialysis membranes with an area of 6.6 cm^2. The aqueous source phase was 250 ml of 0.5 M HCl with 1.0 mM Pb(II) and Cd(II). A 0.10 M chloroform solution (10mL) of tetra-n-heptylammonium chloride (THAC) was the membrane phase. The aqueous receiving phase (25 ml) was pure water. Selective permeation of Pb(II) and Cd(II) was observed. The enrichment factor (EF) (metal ion concentration in the receiving phase divided by metal ion concentration in the source phase) for both heavy metals increased with time and reached values of 4.4 and 0.9 for Pb(II) and Cd(II) respectively after 26 h. In another development, Hayashita et al. (35) used a BLM technique with polymeric membrane having anion-exchange sites (anion-exchange membrane) in permeation experiments with a cylindrical glass cell similar to the BLM cell. The anion-exchange membrane (Selemion AMV, Asahi Glass Co. Ltd.) was attached to the bottom of the cell (membrane area, 1.1 cm^2) and the cell, which contained 5.0 ml of pure water as receiving phase, was dipped into 97 ml of the source phase containing $MgCl_2$ and 0.1 mM Cd(II) and Zn(II) ions. The EF value after 40 h reached 5.8 for Cd(II) and 1.2 for Zn(II) when concentration of chloride ion in the source phase was 0.5 M. As expected, the observed permeation was low as compared with the liquid membrane separation using tetra-n-heptylammonium chloride (THAC) as the membrane carrier in the previous experiments. The authors claimed that this was the first example of the polymeric membrane that exhibits a selective carrier mediated transport for heavy metal ion separation where selectivity was comparable to the liquid membrane separation. Lastly, Hayashita (33) developed a polymeric plasticised membrane for heavy metal separation which is composed of cellulose triacetate (CTA) as a membrane support, o-nitrophenyl octyl ether (NPOE) as a membrane plasticiser, and trioctylmethylammonium chloride (TOMAC) as an anion-exchange carrier. The plasticiser (NPOE) solubilised in the membrane acts effectively as an organic medium for the carrier mediated membrane separation (36-37). The permeation experiments were conducted in a three compartment cell with a large membrane area (15.0 cm^2). The source and receiving phases were circulated from reservoirs through the two outer compartments. The EF values reached 12.0 for Pb(II) and 6.4 for Cd(II) after 5 h. Using a cylindrical dialysis cell, the EF for both heavy metals increased with time and reached values of 13.3 and 0.7 for Cd(II) and Pb(II) respectively after 6 h. The permeation selectivity for Cd(II) and Pb(II) was affected by the large dialysis cell membrane area. In the polymeric membrane separation, the time required to achieve an EF of 5.8 for Cd(II) is around 40 h, whereas with a polymeric plasticiser membrane this value was achieved in 2 h. Thus, it is evident that the polymeric plasticiser membrane exhibits superior transport efficiency and selectivity over the conventional polymeric anion-exchange membrane.

To enhance hydrophobicity of the liquid membrane carrier using azacrown compounds, Shamsipur et al. (38) reported the cooperative transport of some metal ions through liquid membranes containing a mixture of azacrowns and fatty acids (38-40). They report that the addition of long chain fatty acids to the membrane phase not only significantly reduces the degree of carrier loss, but exerts a cooperative effect on the uphill transport of metal ions through liquid membranes (38-41). Recently, they reported the transport of Cd^{2+} ions through a liquid membrane containing a mixture of aza-18-crown-6 and palmitic acid. Transport of Cd(II) cation was around 94% using sodium thiosulphate as the receiving phase. Selectivity was reported to be better in the presence of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and Ag(I) as well as alkali and alkaline earth metals. To eliminate the interference of Cu(II) and Ag(I) ions, they were masked by thiocyanate in the source phase and their interference in permeation could be eliminated. The hydrophobicity of carriers was reported to be enhanced but these studies did not provide long term stability of the cooperative carrier liquid membrane systems. The proposed mechanisms of metal transport were inadequate to explain the cooperative effect since addition of fatty acids to the azacrown ether would increase the viscosity and density of the membrane phase. The metal ion diffusion coefficient through the membrane phase should be calculated at the concentration of fatty acids added to the azacrown ether phase.

Supported liquid membranes (SLMs)

An organic liquid containing an active complexing agent (carrier) in suitable diluent can be impregnated in the pores of a porous polymeric solid support by capillary action. This membrane solvent should not mix with water. The membrane is clamped between two cells which are filled with an aqueous source and receiving phase. The aqueous solutions are constantly stirred either mechanically or magnetically in order to achieve homogeneity and reduced thickness of the stagnant aqueous layers. This form is usually designated as an immobilised liquid or supported liquid membrane (SLM). An SLM technique not only has considerable significance for laboratory practice but is also of interest for a range of technological purposes because of the large phase boundaries which are attainable. Published reports (42-43a) detail a range of SLM system arrangements. The most important are briefly described here. A planar or flat geometry is very useful for laboratory purposes. For industrial purposes, a planar geometry is not very effective since the ratio of surface area to volume is too low. Hollow fibre and spiral wound modules can be used to provide high surface area to volume ratio. Usually a set of some hundreds of hollow fibres are used in a standard module. The organic carrier solution is held within the pores of the membrane. The source and receiving phases are inside and outside the hollow fibres respectively, or vice versa. In the following section, more attention is paid to continuous processes such as HFSLMs under the heading "Supported liquid membranes". The flat sheet supported liquid membrane, in general, is not discussed unless there is some new or significant improvement in the system. A number of papers on FSSLMs are discussed while describing the modelling of the transport process owing to their theoretical importance.

Non-despersive membrane based extraction

There is a continuous improvement in configurations of hollow fibre modules manufactured by Hoechst Celanese (Liqui-Cel). Recently, non-dispersive solvent extraction was carried out for the recovery of Au(III) from alkaline cyanide media using LIX 79® as organic extractant. The separation factor of Au(III) over base metals such as Cu(II),Zn(II) and Fe(III) was reported very high. The hollow fibre module contactor with polypropylene support having surface area of 1.4 m^2 was used in this study. More than 90% of the Au(III) was extracted in presence of large amount of Cu(II) and Fe(III). The process has been patented in 1998 by Kumar et al. (43b). Similarly, environmental point of view, removal of toxic heavy metals such as Cu(II), Cd(II) and Zn(II) from waste water was reported by Kumar et al.(43c) using dispersion-free hollow fibre membrane extraction process . The organic extractant used for copper extraction was 0.1M Cyanex 272 in n-heptane. The Cd(II) and Cu(II) were extracted together between pH 3.8-4.0 and Zn(II) in pH range of 2.0-2.5 from aqueous solutions. It was possible to achieve extraction of metals in the range of 80-90%. In both the studies, more attention was paid to maintain higher pressure in the aqueous stream than the organic stream in order to prevent organic stream wicking into the aqueous phase. The pressure difference was between 0.2 kg/cm^2 to 0.6 kg/cm^2 (43c). Likewise,, the extraflow type of hollow fibre modules were used by Plucinski et al. (44). In their studies, hollow fibre membrane extraction of Cd(II), Ni(II) and Zn(II) with bis(2-ethylhexyl) phosphate (DEPA) in isododecane was performed and it was possible to achieve a decrease in metal concentration of 2-4 orders of magnitude in the aqueous phase by extraction in a single-pass flow mode. The concentration range of DEPA was between 0.05 and 0.5 M. For stable operation of the HF module, the authors paid attention to maintaining higher pressure in the aqueous phase (0.2 bar) than in the organic phase so as to ensure that the organic carrier stayed in the pores of the membrane. The concentrations of Cd(II), Ni(II) and Zn(II) were in the range of 10^{-5} to 10^{-4} M and aqueous phase initial pH was 4.8 to 5.5. The results for extraction were compared with those for a pulsed sieve-plate column and ideal mixer-settler cascade. It is noted that one module (54 cm long and 9,000 fibres, or 25 cm and 10,000 fibres) can replace the extraction column of 6 m in length and two to four ideal stages. The experiments conducted with waste water demonstrated the possibility of a thousand-fold enrichment of zinc starting from 100 mg/l. The permeation model for calculating mass transfer coefficients is also presented. Although the studies show the potential of using the hollow fibre module (HFM) for environmental applications, long term use of these modules and solubility of extractant to the aqueous streams need to be tested in order to check pollutant concentration in the waste water. Similarly, from an environmental point of view, cadmium removal from phosphoric acid using HFM modules was reported by Alonso et al. (45). Their objective was to reduce cadmium levels in fertilisers, which are currently a serious environmental problem. The batch non-dispersive solvent extraction of Cd(II) using Cyanex 302 in kerosene was examined with two modules, i.e., a hollow fibre module for extraction and a ceramic module for the stripping step (due to high acidity of the strippant), together with three stirred tanks for homogenisation of the fluid phases. The aqueous feed which passed through the extraction cell (shell side) contained Cd(II) in the range of 4.4 10^{-3}-5.6 10^{-3}M. The carrier Cyanex 302 concentration was 5% v/v in kerosene. The flow rates of aqueous feed and organic carrier solution in the extraction module were 1.8 10^{-2} m^3/h and 2.34 10^{-2} m^3/h respectively. In the back extraction module, organic and aqueous stripping agent (6 M HCl) circulates though the channels in the ceramic support at the rate of 2.34 10^{-2} m3/h and 2.16 10^{-2} m^3/h respectively. To ensure that no displacement of the organic carrier from the pores of the membrane takes place, the authors took the precaution of maintaining the aqueous phase 4 psi (~0.3 kg/m^3) higher than the organic phase. The mass transfer model of cadmium is presented, and experimental values are in accordance with simulated values. The mass transfer coefficients reported are: K_{me} = 8.33 10^{-8} m/s and K_{ms} =

3.33 10^{-8} m/s, p = 2 (number of Cyanex 302 aggregated) and Kė = 6 103 mol $^{-2}/l^{-2}$. The simulation of a batch process in order to reach a 95% separation efficiency of the cadmium containing phosphoric acid was carried out and results are reported to be promising.

Analytical applications of SLMs and HFSLMs

Different enrichments techniques have been described for the determinations of trace level of metals from aqueous solutions. Sample preparation methods based on liquid-liquid extraction are now gradually being replaced by either solid-phase extraction or supported liquid membranes (25). The latter proved to be more compatible because of simplicity of the technique. Further, SLM methodology appears to be very modern approach to sample clean up and enrichment specially when metal concentrations are at ultra trace level. The use of hydrophobic polymers as a support for an organic phase has been proposed by several investigators including Warshawsky, Pohlandt et.al. and miller et.al. (24). Recently, studies on SLMs and HFSLMs have been reported which are related to the analytical importance of the technique (22-26). In a similar development, an SLM system for the separation and concentration of vanadium(V) was tested and characterised by using tricaprylmethyl ammonium chloride (Aliquat-336) dissolved in dodecane as carrier (22). The transport of vanadium through the liquid membrane is based on a pH gradient between the feed and stripping solutions to provide an appropriate change in the chemical species of aqueous vanadate, i.e., aqueous metavanadate, $VO_2(OH)_2^-$ (4.0 <pH <7.0), is extracted by Aliquat-336 whereas species VO_3OH^{2-} (pH >8.0) were unextractable. Initial feed solutions of 5 mgL^{-1} vanadium(V) at pH 6.0 and 0.1 M of ionic strength and stripping solution of 0.5 M ammonia in a 0.1 M of ammonium nitrate were used. The organic solution at the membrane phase was 0.15 M of Aliquat-336 dissolved in a dodecane/dodecanol mixture. Transport of vanadium(V) increases with the flow rate of the feed solution through the fibre until a "plateau" is reached (>0.2 ml min^{-1} in a single fibre). The probable reason for this behaviour mentioned by the authors is that the membrane area increases with the number of fibres but there is also an increase in the sterical hindrance between the fibres, which reduces the expected increase of vanadium transport. However, the length of the fibre has little influence on the transport process. It is claimed by the authors that vanadium(V) could be effectively concentrated and selectively separated over Mg(II), Ca(II), Na(I), Mn(II), Ni(II), Cu(II), Cr(VI) and Zn(II) by HFSLMs. In spite of the high reproducibility of the results and the system's analytical importance, no data is presented on stability aspects of the HFSLM system. The flow rates tested seem to be very low, which limits the technique to small volumes of solution. In another study, Buffle and co-workers (23) developed a technique based on HFSLMs consisting of 1,10-didecyl diaza-18-crown-6, fatty acid in a mixture of toluene and phenyl hexane (1:1) as diluent, for speciation of trace metals such as Cu, Pb and Cd for application in natural water conditions. Two types of single hollow fibre modules, i.e., non-flow and flow systems, were used for free metal ion separation and preconcentration. The sample solution consisted of desired concentrations of Cu(II), Pb(II) or Cd(II) nitrate in 10^{-2} M MES adjusted to pH 6 with LiOH. The stripping solution contained 5 10^{-4} mol l^{-1} CDTA adjusted to pH 6.4 with NaOH. The carrier solution 0.1 M 1,10-didecyl diaza-18-crown-6 (Kryptofix 22DD) and 0.1 M lauric acid dissolved in a mixture of phenyl hexane and toluene and the Accurel PP q3/2 (Akzo) hydrophobic hollow fibre (HF) was used as the support for the liquid membrane. The studies were reported to be suitable for obtaining high preconcentration factors under natural water pH conditions for Pb(II), Cu(II) and Cd(II). High preconcentration factors in the range 100-3000 for Cu(II), Pb(II) and Cd(II) were obtained. The time required to achieve this preconcentration ranged between 5 and 120 min when sample and receiver solution volumes were 250 ml and 60 μl respectively. Long term stability of these membranes showed that they are stable for at least seven days of continuous use. The authors claimed that by combining HFSLMs with sensitive analytical dectectors e.g., voltametric ones, detection limits of metal ions below 10^{-10} mol l^{-1} could be achieved. In a similar study, Taylor and associates (24) reported a method for the determination of traces of gold in cyanide process solutions. Preconcentration of dicyanoaurate(I) anion is achieved by extraction into a supported liquid membrane, formed by *in situ* coating of a thin layer of organic phase (1% m/v tridecylamine (TDA) in a diluent consisting of 50% TBP in heptane) onto a polymeric support. This support is packed into a minicolumn (packed with polysorb MP-1, a hydrophobic sorbent based on cross-linked styrene-divinylbenzene with a bead size of 35 μm) which forms part of a flow injection manifold. After the sample solution has flowed over the organic phase for a suitable period, the entire organic phase is washed off the column with an organic solvent and introduced into the flame of an atomic absorption spectrometer. With an SLM approach, it was possible to utilise the rapid kinetics of liquid-liquid extraction to obtain the reproducible preconcentration of gold from cyanide solutions. Using 10 ml of 40 μg/l sample, a 53-fold preconcentration of gold was achieved in a load time of 120 s with a standard deviation of 2.7% and a sampling frequency of 24 h^{-1}. Interfacing a simple flow injection manifold with a flame atomic absorption spectrometer allowed the instrument to be used for determining gold traces in cyanide solution in the range of 0.01 to 0.1 mg/l. Further, a methodology has been developed by Djane and associates (25) to preconcentrate metal ions such as Cu(II), Cd(II) and Pb(II) from reagent water and river water samples using SLMs containing 40% w/w D2EHPA dissolved in kerosene as the membrane solvent and PTFE (Fluoropore FRG) as solid support. The extraction efficiency was reported to be unchanged as long as pH difference across the membrane was more than 2 pH units. The

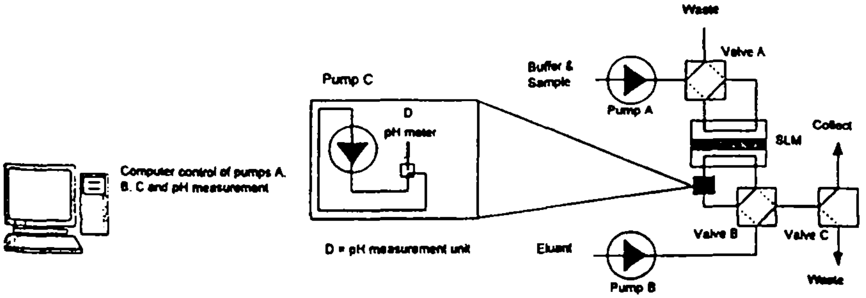

Fig. 4. The schematic diagram of set-up used for on-line monitoring of the SLM based trace metal determination device (reproduced with the permission of Springer-Verlag, Ref. 25).

authors claimed that under optimal conditions, the membrane was stable for at least 200 h with reagent water and at least 80 h for river water samples. Enrichment factors of approximately 15 times could be obtained in the presence of a large excess of interfering ions. The detection limits of blank samples for Cu^{2+}, Cd^{2+} and Pb^{2+} using 120 min processing time were 0.19, 0.024 and 0.09 ng/ml respectively. Fig. 4 depicts the schematic diagram of the set-up used for on-line monitoring of the SLM based trace metal determination device. Likewise, Valiente and co-workers (26) developed an SLM system for the selective separation of selenium from hydrochloric acid solutions using sodium diethyldithiocarbamate Na(DDTC) as a carrier. The membrane phase consists of an organic solution of TBP or kerosene and Na(DDTC) in the feed solution that acts as a selenium carrier. Stripping of selenium was performed from the organic phase using hydrogen peroxide in hydrochloric acid. The presence of H_2O_2 in the stripping solution was considered necessary to accomplish the mass transfer of selenite. The transport of Se(IV) was reported to be selective for Se(IV) and Cu(II) in the presence of Mg(II), Fe(III) and Ca(II) when the source phase was constituted by 1.14 10^{-4} M selenite solution in 2.25 10^{-3} M hydrochloric acid and Na(DDTC), 4.44 10^{-3} M and stripping solution 0.24 M H_2O_2 in HCl. The spectrophotometric measurements were performed in order to elucidate the chemical mechanism of Se(IV) transport. The spectra of the corresponding organic solutions after contact with either feed or stripping solutions are depicted in Fig. 5.

Sandwich SLMs

The possibility of performing multistage separation of metal cations using a series of composite liquid membranes was first proposed by Danesi and co-workers (46-48). In all these sandwich

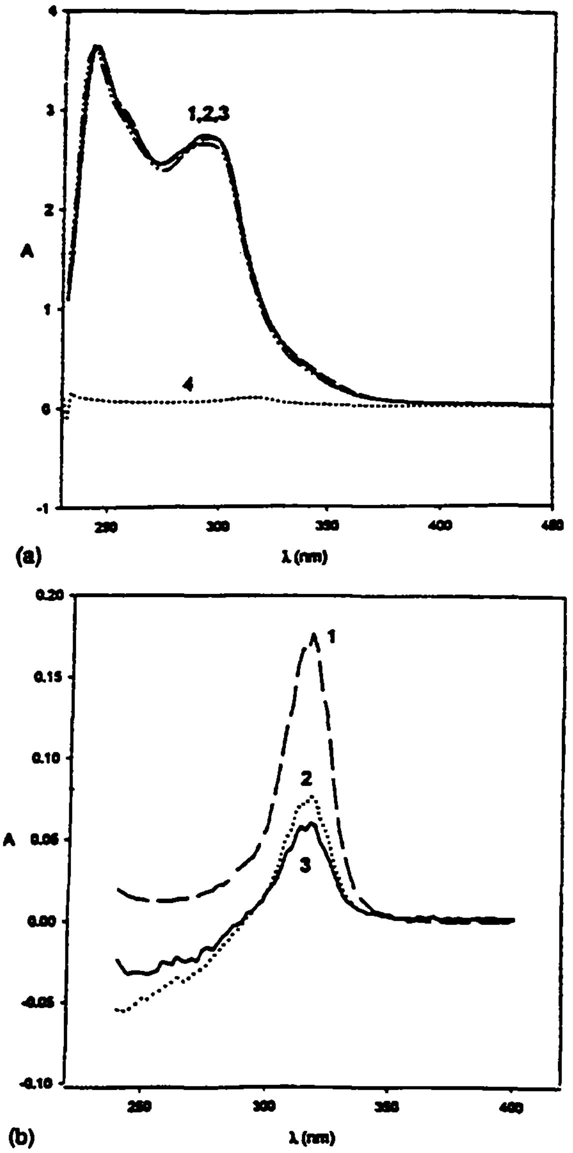

Fig. 5. Spectra of the corresponding organic solutions after contact with either feed or stripping solutions, where: (a) (1) extracted complex, (2) after stripping with 0.24 M H_2O_2, or (4) after stripping with a mixture of HCl and H_2O_2 at the mentioned concentrations; (b) (1) CS_2, (2) after stripping of the complex, and (3) after stripping of DDTC (reproduced with the permission of Elsevier Science, Ref. 22).

SLMs, stripping solution of the first membrane is chosen to promote the extraction of a metal ion into the second membrane. A composite SLM for the ultra clean separation of Co-Ni (46), multistage separation of Eu^{3+} from Am^{3+} (47) and the use of complementary SLMs for the permeation of Eu^{3+} and Am^{3+} (48) have been described in detail. However, in spite of the better performance of composite SLMs, relatively few papers have been published on this subject. Recently, the transport behaviour of Mo(VI) across a membrane impregnated with LIX 63 in kerosene was investigated by Akiba et al. (49) across SLMs and combining this system with an alternate membrane containing trioctylmethylammonium chloride (TOMAC) and 1-octanol (modifier) in kerosene for the better recovery of Mo(VI) through the double membrane (sandwich SLM). The goal of this work was that Mo(VI) could be transported with LIX 63 as MoO_2^{2+} from acidic solutions and stripped into alkaline solutions as MoO_4^{2-}, which is again extractable with a liquid anion exchanger such as TOMAC. Mo(VI) ($5\ 10^{-4}$ M) from 0.1 M HNO_3 could be transported across a LIX 63/kerosene (10^{-2} M) liquid membrane with recovery exceeding 80% in product phase consisting of 0.1 NaOH. Almost complete and selective transport of Mo(VI) from 10^{-3} M HNO_3 was accomplished by double membranes containing 0.1 M LIX63 in kerosene and 1 M TOMAC-10% 1-octanol in kerosene as carriers and 0.05 M NaOH and 1 M NaOH as intermediate and final receiving phases respectively. The high complexing ability of LIX 63 with Mo(VI) in acidic solution provides for its separation from a host of accompanying ions. In another study, Zuo et al. (50) reported a great increase in SLM lifetime when a suitable sandwich SLM was operated. When a hydrophilic lens paper was interposed between the SLM investigated for the copper permeation, a stagnant aqueous layer was reported to build up. According to the authors, no micelles of carrier and water were formed at the interface in this manner, which was previously suspected of causing the decrease in the permeability of the copper.

The membrane's permeability behaviour was observed to be the same with longer membrane life. The theory proposed by Zho et al. was contradicted by other authors in their latest review (30). Similarly, Saito (51) has used a hydrophilic dialysis membrane (15μm each) with a sandwich SLM in order to prevent the loss of membrane solvent and carrier. An SLM made of a porous polypropylene membrane impregnated with a dibenzyl ether solution of bathocuproine (4,7-diphenyl-2,9 dimethyl-1,10-phenanthroline) as the carrier and a composite SLM made of two sandwiched dialysis membranes were prepared by the authors to examine zinc ion permeation tests on both membranes. In spite of stability problems, the lifetime for the sandwiched SLM was higher than that of the single stage SLM. However, the permeation velocity of Zn(II) declined significantly with the sandwich SLM as compared to a single stage SLM. The permeation velocities with single stage SLMs and sandwich SLMs were reported to be $4.9\ 10^{-11}$ mol cm^{-2} s^{-1} and 1.2110^{-11} mol cm^{-2} s^{-1} respectively. The sandwich concept of SLM has potential but should not be employed at the cost of declining metal ion permeability and poor membrane stability.

Gelation of SLMs

A gel is a form of matter that is intermediate between a solid and a liquid. It consists of polymers or long-chain molecules cross-linked to create a tangled network and immersed in a liquid medium. The liquid prevents the polymer from collapsing into a compact mass; the network prevents the liquid from flowing away (52). With this concept in mind, Bloch et al. (53) first proposed the idea of gelled membranes. They made an attempt to extract uranium by polyvinylchloride (PVC) which was plasticised with several phosphate esters which acted as an extractant. According to these authors, the lifetime of these membranes was not long enough and the permeability of metal ions was affected owing to extractant washout from the membrane film. Nevertheless, other authors claimed (54-55) that these solvent polymeric membranes, which consist of a polymer film containing a plasticiser, have high stability and durability even though they show a low ionic permeability compared to other types of membranes. This is because the transference of the carrier in the membrane is depressed by its high viscosity and high diffusional resistance. Accordingly, ionic permeability may be improved by selecting the appropriate plasticiser. The authors (54) investigated the permeability of zinc across cellulose triacetate membranes (CTA) containing bathophenanthroline (4,7-diphenyl-1,10 phenanthroline) as a carrier with various plasticisers and their mixtures. The value of metal flux and thickness of membrane was reported to be proportional to the diffusion constant in the membrane when tris(2-n-butoxyethyl) phosphate, TBEP in o-nitophenyl-octyl ether (NPOE) plasticiser was used with carrier. The flux values of zinc across CTA containing bathophenanthroline and various plasticisers are shown in Table 1. In another study, Sugiura (55) reported the fluxes of lanthanides across CTA membranes by using mixtures of NPOE and a series of n-alkyl ethers (POE ethers) as plasticisers and hinokitiol (β-isopropyltropolone) as carrier. Effects of alkyl and polyoxyethylene (POE) chains of this ether on the flux were examined and lanthanide transport was found to be coupled with a flow of hydrogen ions. The POE ethers used [$C_nH_{2n+1}(OCH_2CH_2)_xOH$, referred to as C_nE_x] were $C_{10}E_3$, $C_{12}E_3$, $C_{14}E_3$, $C_{16}E_3$, $C_{12}E_2$, $C_{12}E_4$, $C_{12}E_6$ and $C_{12}E_8$. The high fluxes were observed for the lanthanides from samarium to lutetium while the fluxes for lanthanum to neodymium were reported to be extremely low. The flux for lanthanides was found to decrease with an increase in POE chain length. Neplenbroek et al. (56-58) used gelation of the LM phase to stabilise the SLMs, which they carried out assuming that only emulsion formation is responsible for the degradation of SLMs. The gelled liquid membranes with low polymer concentration are interesting for practical applications because the

Table 1

Fluxes of zinc ion across the cellulose triacetate membranes containing bathophenanthroline and plasticisers

No.	Plasticiser[a]	Zinc-ion flux[b] 10^7 (mol $cm^{-2}h^{-1}$)
1.	*o*-Nitrophenyl phenyl ether (NPPE)	1.03
2.	*o*-Nitrophenyl n-octyl ether (NPOE)	0.76
3.	*o*-Nitrophenyl n-heptyl ether (NPHE)	0.74
4.	Tris(2-n-butoxyethyl)phosphate (TBEP)	0.50
5.	Tris(ethylhexyl) phosphate (TEHP)	0
6.	Tri-m-tolyl phosphate (TMTP)	0.27
7.	Di-n-butyl phthalate (DBPT)	0.33
8.	NPOE-TBEP	1.46
9.	NPOE-TEHP	1.17
10.	NPOE-TMTP	0.66
11.	NPHE-TBEP	1.17
12.	NPHE-TEHP	0.94
13.	NPHE-TMTP	0.43
14.	NPPE-TBEP	1.58
15.	TEHP-TBEP	0.52
16.	TMTP-TBEP	0.83
17.	DBPT-TBEP	1.00

a, Plasticisers 8 to 17 are 1:1 mixtures.

b, Mean values in the range of 1 to 5 h after the start of the zinc-ion transport.

Source: Ref. 54

diffusion rate of carrier molecules in a gel network decreases drastically with increasing polymer content. By gelling the membrane liquid, its macroscopic viscosity increases and the resistance against liquid displacement from the support is enhanced. The prevention of deformation of the LM meniscus helps in preventing emulsion formation. As a result, the SLM is more stable. The stabilisation of the liquid membrane by gelation with PVC was carried out in a number of ways and in their experiments mechanical stability of the membrane improved as LM loss was reduced. In another gelled membrane, a thin cross-linked gel layer with a higher polymer content (40%) was applied at the feed side of the membranes and effectively suppressed SLM degradation which was caused by emulsion formation. The authors report that this treatment has no negative influence on flux because the dense gel layer was relatively thin and in addition very high stability for more than a year was predicted for practical applications. This was predicted by a model but stability for 9 weeks have been claimed with experimental findings. When experiments were conducted to remove nitrate ions by this LM system, the initial nitrate flux was less when PVC concentration was increased in the membrane formulation. The reason for this given by Neplenbroek et al. was an increase in the tortuosity factor on gelation of the LM phase (56-58). It is proposed by the author (58) that development of stable SLMs resulted from a composition of the LM phase chosen in such a way that it has little capacity for emulsion formation. The structure of the carrier is of great importance. Furthermore, instability can be diminished by varying the composition of the aqueous phases. In practise, the boundary conditions are determined by the total process occurring in the SLM system. Unless, scaling up studies of gelled membrane are reported, macroscopic behaviour of such membrane can not be predicted. Further, large scale fabrication of gelled membranes are doubtful as surface properties of such membranes should be uniform in order to obtain stable LMs. Thus, more detailed studies are required to evaluate gelled membranes in terms of membrane stability and high metal transport. The scope for industrial application of gelled membranes would seem to be limited owing to these uncertainties.

Dual module hollow fibre membrane

Dual module hollow fibre (DMHF) systems are similar in configuration to SLMs but they differ in impregnation as solvent is not confined to the pores of the plastic layer. Feed and receiving phases flow through hollow fibre lumens. The fibre area which is always in contact with organic solvent containing carrier is large. The possibility of losing membrane integrity owing to solvent loss is minimised during permeation of metal ions. The source phase generally flows through one set of fibre lumens and the receiving phase flows through a second set which is immersed in the organic phase. Transport occurs as the target cation diffuses through source phase fibres and enters the bulk organic phase that contains the carrier. The cation permeates across the receiving phase fibres where it enters the aqueous receiving phase. Izatt et al. (59) state that this system has potential for practical applications owing to improved stability. One disadvantage is the possibility of membrane pores fouling up as a result of surface effects caused by continuous contact of the organic carrier with the membrane. Highly hydrophobic solvents and carriers must be chosen for optimal membrane function. A similar set-up was used recently for the preconcentration of metal ions and assay (23).

Design of ion specific carriers in liquid membranes

Liquid membranes incorporating host species can effect rapid and selective transport of a variety of guest species and have wide applications in sensing and separation processes (60). Since the carrier dramatically improves transport performance, development of new, specific carriers is the most exciting task in liquid membrane science and technology (61-62). This section describes new tactics in carrier chemistry, strategies and concepts in the design of powerful carriers which are specific for some metal cations.

Molecular design of new, specific carriers is a rapid method to create practical liquid membrane separations, although it usually includes empirical "trial and error" excercises. Tsukube (63) and Grootenhuis et al. (64) have reported that computer chemistry proved to be a very effective methodology in the design of specific carriers and a rational basis for carrier synthesis. Although there are three kinds of computational methods, empirical, semi-empirical and non-empirical calculations, bench chemists have limited themselves to the use of empirical methods such as MM2 and have rarely employed semi-empirical or non-empirical calculations in carrier chemistry (65). First, the standard convention is that molecular simulation refers to calculations using force fields such as Monte-Carlo and molecular dynamics. Computation chemistry generally refers to calculations that solve the Scrödinger equation using some kind of approximation (Hartree-Fock, density functional, semi-empirical). MM2 refers to a force field used for molecular mechanics calculations. The MNDO,AM1, and PM3 methods refer to semi-empirical quantum mechanics methods. Tsukube (65) reported a new approach for the development of specific carriers in liquid membrane as: (i) computer-aided design of cation specific carriers and (ii) functionalisation of rare earth complexes as anion carriers. The author designed Li(I) and Ag(I) ion specific carriers using MM2,MNDO (computer software) and density functional calculations. The carrier was selected from a variety of acylic podands, cyclic crown ethers, bicyclic cryptands and related derivatives. The author applied the "extended MM2 program" (CAChe Scientific, version 3.0) to design Ag(I) ion specific carriers (66). A podand type carrier was chosen which has three pyridine moieties as potential binding sites for Ag(I) ion

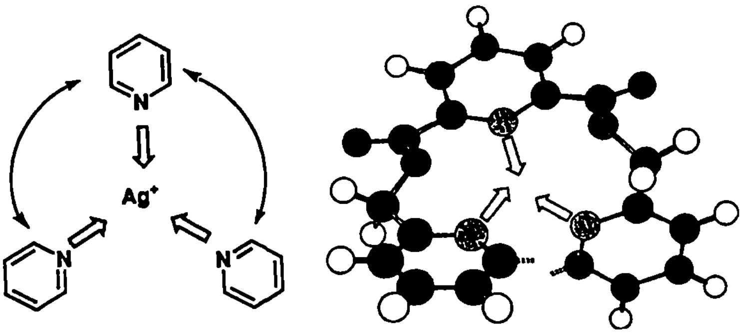

Fig. 6. Optimised structure of podand by extended software MM2. Two substituents and the Ag$^+$ ion are omitted for simplified illustrations (reproduced with the permission of Elsevier Science, Ref. 66).

(Fig. 6). On the other hand, Tsukube and co-workers (67) applied non-empirical "density functional calculation" to design Li(I) ion specific armed aza-12-crown-4 derivatives (Fig. 7) (67). "Armed crown ethers" are a new type of cation carriers and are characterised by a parent crown ring and a cation ligating side arm (68, 69). Such ionopores exhibit both the kinetically fast complexation properties of simple crown ethers and the three-dimensional binding characteristics of the bicyclic cryptands. These features were similar to those of naturally occurring ionophores and offer effective binding and selective transport of target metal cations. The guest selectivity could be tuned by selection of the crown ether ring and the side arm and several armed crown ethers were reported to show high guest selectivity and excellent transport efficiency. Although there are still many problems to be resolved, computer chemistry could be a good partner for work in carrier chemistry.

In another study performed by Dozol and co-workers (70), calixerenes were selected for the removal of caesium from nuclear waste because of their specific structure. Selective permeation of Cs$^+$ from 1 M HNO_3 was accomplished across SLM in the presence of a very large amount of sodium using 1,3-calix[4]-bis-o-benzo-crown-6 and 1,3-calix[4]-bis-naphthyl-crown-6 in NPOE as carrier and deionised water as receiving solution. Decontamination factors (defined as the ratio of caesium activity in product, μCi/ml to caesium activity in feed, μCi/ml)greater than 20 were reported with synthetic acidic nuclear waste with the membrane stability over 50 days.

To improve the performance of carriers in the LM, DEHPA was added with macrocyclic crown compounds (dioxo-13-crown-4, 13-crown-4, benzo-4-crown-4, 15-crown-5 and benzo-18-

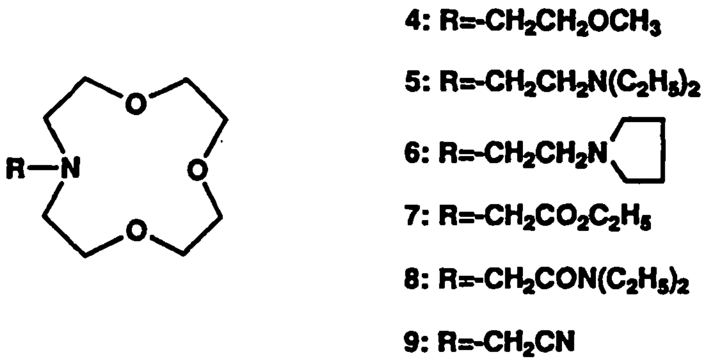

Fig. 7. Armed crown ethers as Li^+ ion-specific carriers (reproduced with the permission of American Chemical Society, Ref. 63).

crown-6) having (benzyloxy)methyl and (benzoyloxy) methyl groups (71). In permeation experiments, the source phase consisted of 0.1 M of LiOH, NaOH and KOH solution and the membrane was chloroform solution of 0.005 M of crown ether and DEHPA and receiving phase 1 M HCL. Substituted 15-crown-5 and benzo-18-crown-6 derivatives/DEHPA mixed carriers showed significantly enhanced transport of Li^+ and Na^+ compared with those of 15-crown-5/DEHPA and benzo-18-crown-6/DEHPA. It was reported that the introduction of a side arm such as the (benzoyloxy) methyl group to the crown ring easily modified the selectivities of the alkali metal cations in these mixed carrier systems.

Hollow fibre contained liquid membrane

Before describing the HFCLM, it is important to understand the instability aspects of SLMs. The probable causes of the instability of the SLM were identified by Danesi (72) as:

- loss of extractant by solubility in mobile feed and stripping solutions
- progressive wetting of the support pores by surface-active carrier molecules
- pressure differential across the membrane exceeding capillary forces holding the liquid

In addition, a large osmotic pressure gradient across the SLM due to an ionic concentration variation between the feed and the strip tends to make the SLM unstable and leads to considerable flow of water across the membrane. Low SLM stability is highly likely in a system with low solvent interfacial tension and high aqueous-organic mutual solubility. The most efficient carrier molecules incorporated in solvents for selective transport always contain surface

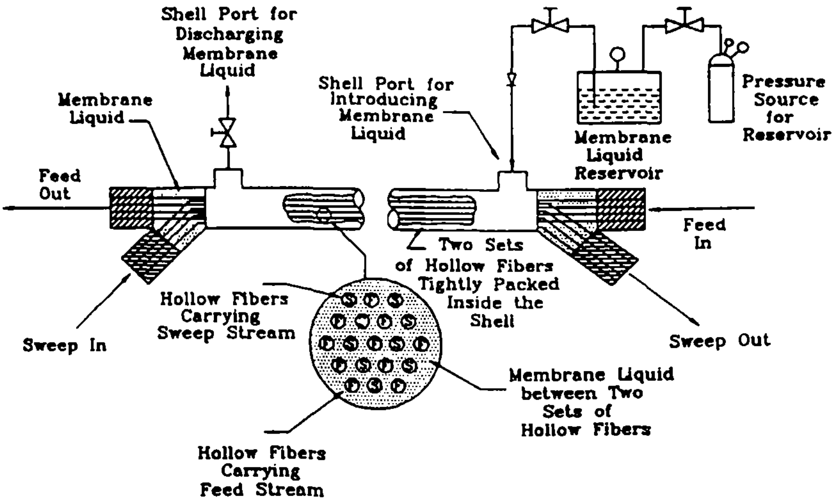

Fig. 8. Basic hollow fibre-contained liquid membrane (HFCLM) permeator structure (reproduced with the permission of American Chemical Society, Ref. 15).

active properties (73). In further studies, Babcock et al. (74) tried to eliminate instability by means of thickening or gelation of the liquid membrane but did not succeed. Hence, a new liquid membrane configuration such as the HFCLM, which is stable and able to retain the inherent SLM advantages, is of great interest. The recently developed HFCLM techniques seem to provide practical solutions for improving stability. HFCLMs contain two groups of hollow fibres in the hollow fibre module, that is, the feed and recovery phases are fed into the lumens of the hollow fibres of each group separately, and the membrane phase is continuously fed into the outer side of the hollow fibres of both groups, as shown in Fig. 8. For the recovery of Cr(III) and Zn(II), Teramoto et al. (75) developed the spiral-type flowing liquid membrane module, which is similar to the HFCLM and exhibited no fouling of the membrane function. The flowing liquid membrane was operated for the separation and enrichment of Cr(VI) in aqueous solutions using tri-n-octylamine as the carrier. The mass transfer of Cr(VI) was evaluated by the following equation:

$$[M]_{F,out}/[M]_{F,in} = \exp\left(-k_{FM}S/\upsilon_F\right)$$

where S is the effective membrane area (m^2), k_{FM} the mass transfer coefficient (m/s), υ_F the flow rate (m^3/s), and $[M]_{F,in}$ and $[M]_{F,out}$ are the metal concentrations in module inlet and outlet respectively. The spiral-type flowing liquid membrane module is shown in Fig. 9.

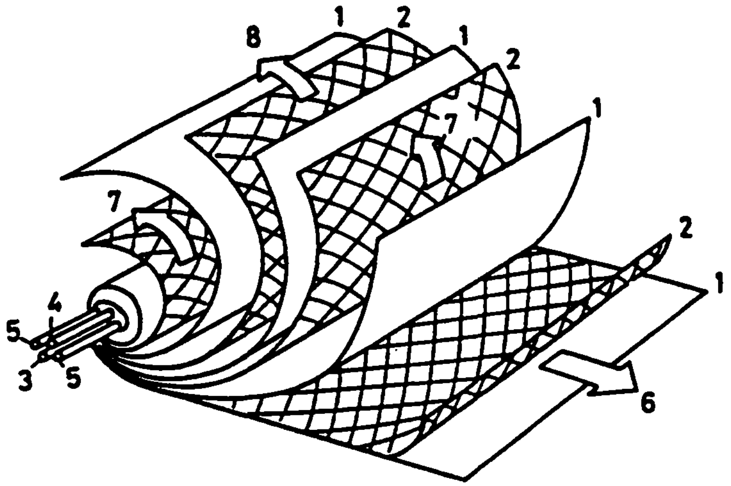

Fig. 9. Schematic diagram of spiral-type flowing liquid membrane module. (1) Microporous hydrophobic membrane (support), (2) mesh spacer, (3) inlet pipe of feed solution, (4) inlet pipe of stripping solution, (5) inlet tube of organic membrane solution, (6) feed solution, (7) organic membrane solution, (8) stripping solution (reproduced with the permission of Marcel Dekker, Ref. 75).

Sato et al. (76) have attempted preferential permeation of Zn(II) from a feed solution of Cu(II) and Zn(II) using 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A) in n-heptane and an aqueous HCl solution for stripping in an HFCLM permeator. In this module, both phases flowed co-currently. The liquid membrane phase was also in slow co-current motion. Overall membrane stability throughout the experiments was reported to be satisfactory. In addition, a study was also made (18) of the performance of a hollow-fibres-in-tube type pertractor consisting of a hydrophilic tube in which a bundle of hydrophobic hollow fibres was inserted. The mass flux per unit volume of the contactor hollow-fibres-in-tube type is higher than in classical bulk liquid membrane contactors and comparable with supported and emulsion-type liquid membrane contactors. Similarly, mass transfer characteristics of HF pertractors (similar to HFCLMs) with two bundles of hydrophobic microporous HF in pertraction of Zn(II) (77) and Nd((III) (78) were determined by Schlosser and co-workers. Mass transfer coefficient values in the pertractor were about 90% greater than those found in solvent extraction from membranes in HF two phase contactor with cross flow of phases and presented in their earlier work (79). Using non-dispersive microporous hydrophobic hollow fibre membrane-based solvent extraction with aqueous waste feed containing Cu(II) and Cr(VI) flowing through fibre bores and organic extractant flowing counter-currently on the shell side, removal of these toxic metals was achieved by Yun et al. (80a). Exit treated stream concentrations of ~1mg/L were achieved with feed stream concentrations of 500 mg/L for Cu(II) or 100 mg/L for Cr(VI). The mathematical model for solvent extraction of copper developed in this study predicted the experimental data well. Further, detailed study of separation and concentration of heavy metals such as Cu(II), Cr(VI) and Hg(II) from their individual aqueous solutions by means of a number of HFCLM permeators was carried out by Guha and co-workers (80b). The studies included both co-transport and counter-transport schemes. The permeation model of Cu(II) was proposed. The concentration of Cu(II) was reduced to sub-ppm level by counter-transport maintaining counter pH gradient among other heavy metal ions, whereas Hg(II) co-transport was performed in a single short (24-48 cm long) module. The system performance was reported to be stable and highly efficient.

Recently, Sirkar and co-workers (81) developed a separation technique using hollow fibre contained liquid membrane modules for the separation of two cations, e.g., Cu(II) and Zn(II), a cation and an anion, e.g., Cu(II) and Cr(VI), and two cations and one anion, such as Cu(II), Zn(II), and Cr(VI). The extraction selectivity of Cu(II) and Zn(II) by LIX 84 (anti-2-hydroxy-5-nonylacetophenone oxime) and D2EHPA respectively in a two-fibre set HFM extractor (one for extraction and another for stripping) is significantly enhanced owing to competitive extraction. The efficiencies of extraction of Cu(II) and Cr(VI) by LIX 84 and tri-n-octylamine (TOA) respectively, are reported to increase owing to self-control of the aqueous feed pH (the protons released from extraction of cations are partly/totally consumed by extraction of anions). In HFM modules, the extraction rates of Zn(II) and Cu(II) by D2EHPA and LIX 84 respectively are controlled by the organic boundary layer resistances as well as the interfacial reaction resistances.

In subsequent studies using the same HFCLM module containing multiple sets of fibres, Sirkar et al. (82) reported the extraction of heavy metallic species Cu(II), Cr(VI), Zn(II) and Hg(II) simultaneously into an appropriate mixed solvent and then recovery and concentration of these heavy metals into an aqueous strippant. In previous studies (81), they had used two separate organic reagents to extract cations and anions but those studies were considered to be excessively complicated because of the typical arrangement of HFCLM fibres for both systems. Therefore, to simplify the process, the idea of mixed solvent was proposed. A mixture of chelating extracting agent LIX 84 and the basic extracting agent TOA in the same heptane diluent simultaneously extracted Cu(II) and Cr(VI) with synergistic effect. On the basis of these results, a three-fibre set microporous hollow fibre contained liquid membrane device was fabricated and used to remove, separate, concentrate, and recover Cr(VI) and Cu(II) from

Table 2

Extraction and separation of Cr(VI) and Cu(II) via a three-fibre-set HFCLM device

Organic membrane composition[a]	Feed flow rate, mL/min	run time, h	pH_{out}	0.1 M NaOH flow rate, mL/min	Cr(VI) in NaOH, ppm	2 M H_2SO_4 flow rate, mL/min	Cu(II) in H_2SO_4, ppm
Extractant 1	2.33	20	3.82	0.28	58.0	0.12	69.0
Extractant 2	1.43	24	3.47	0.36	150.0	0.10	228.0
Extractant 3	1.83	30	3.45	0.49	93.0	0.29	62.0

a, Extractant 1: 5 v/v % LIX 84 and 3.6 v/v % TOA in kerosene. Extractant 2: 25v/v % TOA in kerosene. Extractant 3: 50 v/v % LIX 84 and 25v/v % TOA in kerosene. Feed: Cr(VI) = 220 ppm, Cu(II) = 1000 ppm, pH 4.19.

Source: Ref. 82

synthetic waste waters into separate basic and acidic stripping solutions respectively and simultaneously. The results of extraction and separation of Cr(VI) and Cu(II) simultaneously from synthetic waste water are summarised in Table 2.

Polymeric inclusion membrane (PIM)

Very recently, a novel type of membrane system was developed which couples the properties of rapid transport with high selectivity and ease of set-up and operation. The durability exhibited by such systems is also an important factor for long life. It is interesting to note that in polymer inclusion membrane suitable carrier is entraped in the membrane matrix during the casting process or covalently bounded by chemical method where as in SLM, carrier containing solvent is impregnated on a porous polymer film. Mechanistic point of view, PIM is similar to SLM as described in the following section of the text. In order to improve the stability and selectivity of liquid membranes, Bartsch et al. (21) proposed a new technique to obtain synthetic polymeric ionomer membranes for use in metal separation. They carried out a chemical modification of perfluorinated ionomer membrane material by binding a monoazacrown ether in

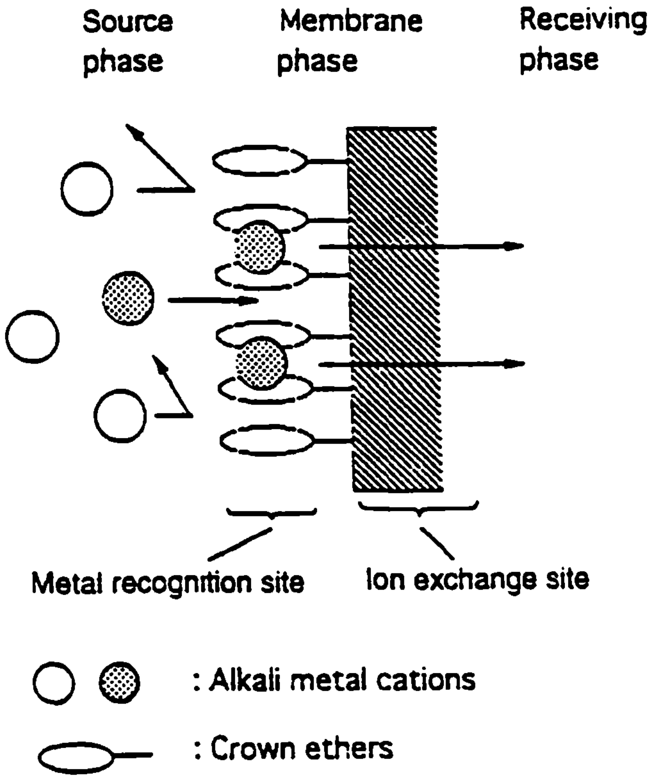

Fig. 10. Alkali metal cation separation by a crown ether-modified Nafion membrane (reproduced with the permission of Elsevier Science, Ref. 21).

the membrane to transport alkali metal cations. The preparation of modified Nafion 117 membrane is described in their studies. According to the ion cluster model for Nafion perfluorinated membranes developed by Gierke et al. (83), the polymeric ions and absorbed electrolyte phase separated from the fluorocarbon are connected by narrow channels about 10 Å in length. This structure has a significant effect on the permeation of alkali metal cations (84). Monoazacrown ethers are considered as potential ionophores for alkali metal cations in solution (85), and were introduced onto the surface of a Nafion 117 membrane (Fig. 10). The objective was to provide barrier layers or channel gates on each side of the membrane through which the metal ion permeation would be controlled by the identity of the ionophoore molecule. The unaltered interior of the Nafion membrane would give efficient metal ion transport between the barrier layers. They first converted the sulphonic acid groups of the Nafion membrane into sulphonyl chloride functions followed by reaction with monoazacrown ethers and some other secondary amines to attach them to the membrane by sulphonamide linkages. For proton-coupled transport, alkali metal cation (Li^+, Na^+, K^+, Cs^+ and Rb^+) permeation is effective when the modified Nafion membranes are derived from acyclic or cyclic secondary amines which contain three or more ethereal oxygens. The authors claimed that the behaviour of the ion exchange membrane changed with respect to each metal ion transported. Since the monoazacrown ether-modified Nafion membranes exhibit good permeation characteristics, it appears that the ionopore molecules were introduced at or near both membrane surfaces to provide barrier layers which influence permeation selectivity for metal cations (21). Sugiura et al. (86-87) presented modelling of PIM prepared by β-diketone containing membranes which are formed by the polymerisation of cellulose triacetate (CTA) to form a thin film. Polymerisation takes place in the presence of a macrocyclic carrier. In thin sheet forms, carrier molecules are trapped within the CTA matrix. The resulting membrane is then placed between the aqueous source and receiving solutions which selectively facilitate transport of a desired metal species from one phase to another. Thus, these membranes do not suffer from loss of organic solvent or leaching of carrier into the aqueous phase, and they are simpler to use than SLMs. Taking into account all the extraction studies performed on PIMs for alkali metal cations by macrocyclic type compounds, there is evidence to suggest that transport across PIMs is carrier mediated: (i) no permeation was observed when the membrane does not contain a macrocyclic carrier, and (ii) the transport selectivity is directly related to macrocycle selectivity. In a recent study, Lamb and co-workers used PIM for the removal of alkali metals such as K^+, Rb^+, Na^+ using DC18C6 (88) and Pb(II) using TOPO as carriers (89). The authors (88) used dicyclohexano-18-crown-6 (DC18C6) bound to the membrane and the order of the binding constants of alkali metal cations with DC18C6 was: $K^+ > Rb^+ > Na^+$. The permeation of these cations through DC18C6-PIMs exhibited similarities with the highest transport observed for K^+ and followed by Rb^+ and Na^+. The carrier mediated transport was claimed to be second order in transport rates with respect to source phase concentration. These PIMs offer several advantages over traditional LMs, including increased flux, the fact that they permit the use of carriers that are less hydrophobic, and their greater durability. Fluxes of PIM are as much as three orders of magnitude higher than comparable SLMs, and PIM separation systems can run for more than three months with little flux variation or membrane deterioration. The author claimed higher fluxes for PIM as compare to conventional supported liquid membrane as thickness of these membrane reported by them is 30 μm. On the contrary the thickness of generally used SLM supports are between 50 to 175 μm like Celgard 2402 (50 μm), Durapore (125 μm) and Flouropure (175μm).

Applications of ion-exchange membrane in metal permeation

The first investigation on ion selective liquid membranes was reported in 1963 by Bloch and co-workers (90). The goals were to eliminate the leachability of the carrier from the membrane and to suppress membrane fouling. For ion extraction, these goals can be achieved by the use of ion-exchange membranes separating the aqueous feed from the organic extraction phase. Many studies on the diffusion of inorganic ions and molecules and the selective transport of metal ions and anions through ion-exchange membranes have been reported by a number of researchers (91-94). Properties of ion-exchange membranes used in liquid membrane application are presented in Table 3 (93). Diffusion and permeation of simple salts in polymers are closely related to the ionic transport phenomena in various systems, e.g., ion exchange, desalination, and biological systems. The transport of ions across membranes is usually regarded as diffusion since it occurs in aqueous solutions (91). The mechanism of the interaction between simple ions and a charged group of a polymer chain is an interesting subject in ion transport phenomena through charged membranes. In a recent study, Ersoz (91) reported the permeability of the charged polysulphonated ICE-450 ion-exchange membrane to elucidate the permselective transport mechanism of alkali metal cations such as Cs^+, K^+, Na^+ and Li^+ as a function of pH. The permeability and diffusion coefficients were found to increase in the sequence $Cs^+ \geq K^+ > Na^+ > Li^+$. In these systems, the metal ions were transported by both diffusive flow based on the concentration gradient and the transport caused by the pH difference between both sides (receiving phase, acid solution with different pH). The transport of metal ions tended to decrease with an increase in the initial pH on the receiving side of the membrane. In the selective transport of metal ions, selectivity depended on both the hydrated ionic size and the interaction between the fixed groups in the membrane and the metal ions. In a similar fashion, the selective permeation of Cu(II) and U(VI) in the presence of a common anion through Nafion 117 ionomer membrane (Nafion 117 perfluorinated sulphonated membrane obtained from DuPont, USA and converted into acid form by refluxing with 1:1 HNO_3) has been reported by Ramkumar and co-workers (92). For the recovery of copper(II), EDTA (0.1 M) was used as the stripping agent, whereas it acted as a masking agent in the source phase for Fe(III), Cu(II), Ni(II) and Zn(II) during the selective permeation of U(VI) using sodium carbonate or Tiron (0.1 M) as a receiving phase. The authors claimed selective permeation of copper from a mixture of iron(III) and copper (II) after masking Fe(III) with F^-, SCN^- and PO_4^{3-} in this system. A lower permselectivity was observed and the permeation of anions was found to be responsible for the simultaneous permeation of Fe(III). It was simply an application of ion-exchange membranes in the permeation studies of metal ions. The permeation mechanism is not presented by the authors,

Table 3

Properties of Ion-Exchange Membranes in Liquid Membrane studies

Type	Supplied by	Thickness (µm)	Ion-exchange capacity (meq/g)
Cation exchange (Neosepta SM-1)	Tokuyama Soda Co., Japan	130-160	2.0-2.5
Cation exchange (NeoseptaCL-25T)	Ibid	150-170	1.5-1.8
Anion exchange (Neosepta AM-1)	Ibid	130-160	1.8-1.2
Cation exchange	Soreq Nuclear Research Centre, Israel	25-27	2.2-3.9
Anion exchange	Toyosoda Co., Japan	160	2.1

Source: Ref. 93

and it is difficult to know the rate determining step for the calculation of the permeation coefficient in their studies. Whether or not these ion-exchange membranes can be categorised as LMs is an issue which must be decided by membranologists.

Emulsion liquid membranes (ELMs)

ELMs which consist of a water-in-oil-in-water system are also known as double emulsions. Two immiscible phases are mixed with a surfactant to produce an emulsion. This emulsion is then dispersed in a continuous phase. Mass transfer takes place between the continuous phase and the inner phase through the immiscible (membrane) phase. In both purification and recovery applications, the ELM must be de-emulsified into two immiscible phases after the extraction step of the process. This is achieved by heating, centrifugation or application of electric fields. The LM phase containing the surfactant and carrier will be recycled to the emulsion preparation step while the internal phase of the emulsion will have the concentrated solute. The main problem associated with ELMs is emulsion breakage. The emulsion must be formulated to withstand the shear generated by mixing during the extraction but must be broken to remove the internal phase and reformulate the emulsion. An additional consideration in the ELM system is water transported along with the solute. This causes permeant dilution in the inner phase, swelling and possible breakage of the emulsion globule. Attempts are being made to modify the surfactant structure in such a way that break-up of the emulsion is minimised, in order to improve the performance of the ELM process. The following section will discuss some details of technological applications of emulsion liquid membranes, emulsion stability, developments of new surfactants and recent advances in break-up of emulsions.

Technological applications of ELM techniques

Recently, significant advances have been reported in applications of ELMs. In addition to the zinc recovery on plant scale in 1986 by Draxler and Marr (95-96), other applications are reported. The details of copper removal from mine solutions (97), removal of selenium(VI) from contaminated ground water (98), removal of heavy metals from effluents (99) and separation of radionuclides from radioactive waste (100) are described below.

(i) *Copper removal*

Field testing of a liquid emulsion membrane system for copper(II) recovery from mine solutions was performed by Nilsen and co-workers (97). The ELM technique successfully demonstrated that copper could be selectively recovered from a range of solutions containing impurity metals and suspended solids. The flow sheet is shown in Fig. 11. Good recoveries of copper were accomplished in these tests (91 to 98%), and satisfactory membrane stabilities were demonstrated. Membrane swelling ranged from 4.1 to 11.4%, and membrane leakage was <1% in all test campaigns. Low levels of organic losses are reported to the effluent from the ELM system (from <3.9 ppm to 11.9 ppm). Pure cathodes from recovered copper were produced from all solutions. The economic evaluation carried out for copper removal by this ELM technique was claimed to be attractive as compared to SX. The parameters and conditions for copper removal by the ELM technique are summarised in Table 4.

(ii) *Waste water treatment*

Removal of heavy metals (Zn(II), Cd(II), Cu(II), Pb(II), and Hg(II)) from waste water is one important application of ELMs. For the removal of heavy metals from waste waters in metallurgical and incineration plants, Marr and Draxler (99) developed the typical ELM process, which they demonstrated in a pilot plant operation. This ELM technique can remove heavy metals efficiently to the level of 99% using di(2ethylhexl) thio phosphoric acid (MTPA), and heavy metal concentration down to 0.2 mg/l Zn(II), 0.02 mg/l Cd(II), 0.007 mg/l Cu(II) and 0.01

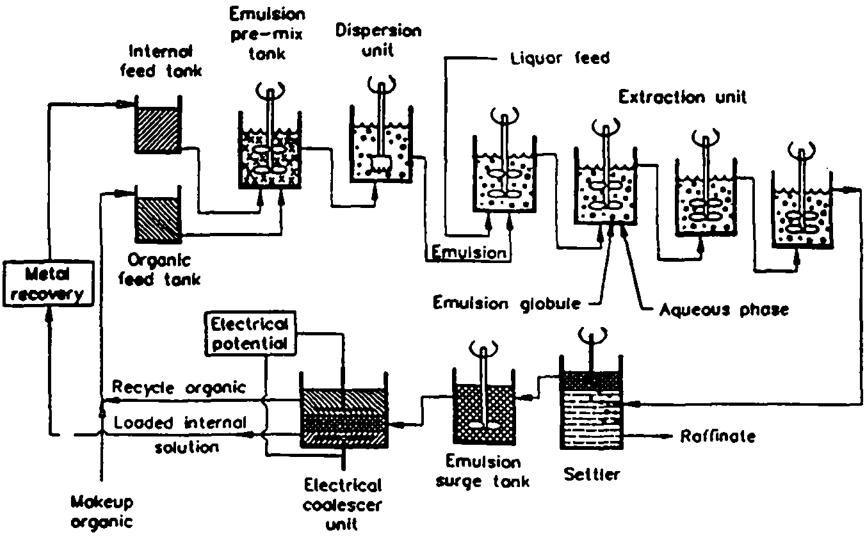

Fig. 11. Simplified flow sheet for the pilot plant scale continuous ELM circuit for copper recovery from mine solutions (reproduced with the permission of American Chemical Society, Ref. 97).

Table 4

Parameters and experimental details for the removal of copper by ELM technique from mine solutions

Organic composition	5.0 to 7.5 wt% Acorga M5640, 1.0 wt%
Surfactant	1 wt% Paranox
Diluent	50-50 Isopar M & V
Lean internal composition	8.5 to 20 g/l Cu
	160 to 165 g/l H_2SO_4
Overall organic/internal phase ratio	4.35 to 4.44
Average internal droplet size	5 μm
Overall retention time in extraction stages	20 h
Total elapsed run time	270 h
Total aqueous feed processed	10,950 gal

Source: Ref. 97

Table 5

ELM system for removal of heavy metals from waste water

External feed phase	230 mg/l Zn^{2+}, 2.7 mg/l Cd^{2+}, 1.1 mg/l Cu^{2+}, 0.5 mg/l Pb^{2+}, pH 3.4
Membrane phase	
Extractant	MTPA
Surfactant	ECA 11522T (polyamine)
Diluent	Shell Sol T (paraffin)
Internal phase	250 g/l H_2SO_4
Efficiency	≈ 99%, 0.2 mg/l Zn^{2+}, 0.02mg/l Cd^{2+}, 0.007 mg/l Cu^{2+}, 0.01mg/l Pb^{2+}

Source: Ref. 99

mg/l Pb(II) can be achieved in the treated stream. The ELM system for the removal of heavy metals from waste water is shown in Table 5.

(iii) *Removal of selenium(VI) from ground water*

Recently, a detailed study was presented by Wright and co-workers (98) for the removal of selenium from contaminated solutions, and they report that it is possible to extract both Se(IV) and Se(VI) from the aqueous waste streams containing large amounts of innocuous anions such as sulphate. The membrane phase is composed of extractant, surfactant and kerosene solvent and n-decanol co-solvent (no details of extractant and surfactant are provided as the authors used proprietary materials). The experiments performed showed that the extraction rate and efficiency depend primarily on the oxidation state of the selenium and subsequently on the pH of the aqueous phase. The process used could rapidly reduce aqueous phase selenium concentration from 1mg/l to a level below 0.01 mg/l (within 15 minutes of contact time), with a concentration factor of 40 in the product phase. After performing the batch extraction experiments, a counter-current extraction column was operated with improved rates of extraction of selenium due to the higher driving force at low concentrations. The authors claim better stability of emulsion in counter-current column experiments. The schematic diagram of an agitated continuous counter-current extraction column is shown in Fig. 12.

(iv) *Removal of radionuclides from nuclear waste streams*

ELMs can be used potentially for the removal of radioactive materials such as strontium(II),

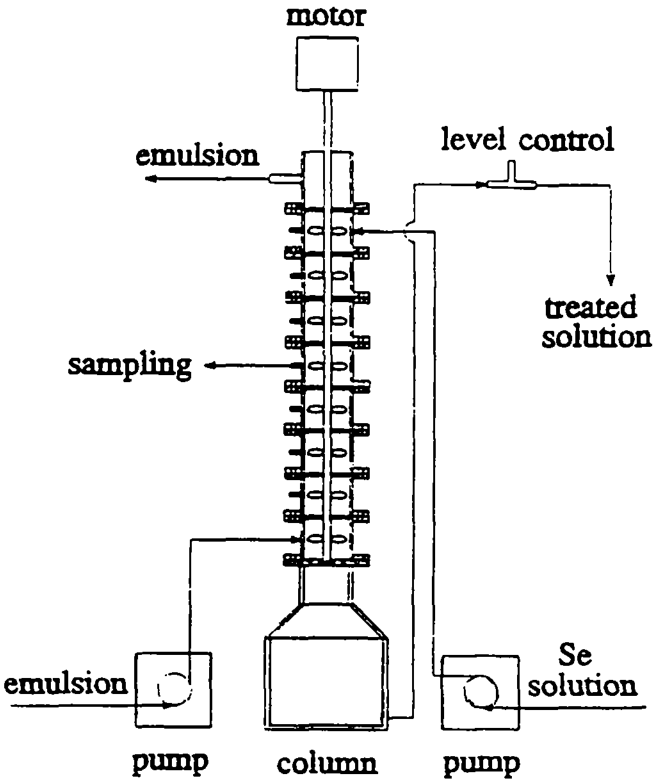

Fig. 12. Schematic diagram of the counter-current extraction column used in the ELM system (reproduced with the permission of American Chemical Society, Ref. 98).

plutonium(IV), cesium(I), uranium(VI), and americium(III) from nuclear waste streams (100). Since a comprehensive review of the recovery of radionuclides by LMs has already been published by Shukla and co-workers (43), this section will only review the latest published papers. Eroglu et al. (101) reported an ELM system for the removal of strontium and about 92% of Sr^{2+} from a feed containing 100 mg/l Sr^{2+} by the use of 0.2 M D2EHPA as extractant, kerosene as diluent and 3 wt% Span 80 as surfactant. The internal phase was HCl at pH 1.6 and the external feed phase was at pH 5.3. In a recent work (102), El-Reefy reported recovery of U(VI) and Th(IV) from Zr(IV), Ce(III), Fe(III), Cu(II) and Cd(II) in a nitrate medium using trioctylphosphine oxide (TOPO) as a carrier. The permeation results showed that it is possible to recover 98% of U(VI) and 82% of Th from 0.1 M HNO_3 solution containing diverse ions. The liquid emulsion was prepared from a TOPO / Span 80 / sodium citrate solution. The recovered U(VI) and Th(IV) was contaminated with less than 2% of Fe(III).

Advances in emulsion formulation

Relatively little attention has been paid to the development of suitable surfactants, in spite of this being a key issue. For the sake of brevity, only the role of surfactants in ELM processes and the development of suitable surfactants for liquid surfactant membranes are reviewed. It is well known that surfactants play an important role in the behaviour of the emulsion in a stirred tank, that is, in the stability of the emulsion globules and the extraction rate of metals by the emulsion globules. There are many papers concerning the effect of surfactants on emulsion behaviour. Mikucki et al. (103) reported that there was an optimum value in the surfactant concentration with respect to the stability of the emulsion and the kinetics of metal extraction, and that this optimum value closely depended on the type of surfactant used. In most studies, however, commercial surfactants such as Span-80 and Polyamine were used. These commercial surfactants are mixtures of more than one compound. To obtain more definite information concerning the effect of surfactants on the behaviour of the emulsion in an ELM technique, it is necessary to use a pure surfactant. The list of synthesised surfactants, their break-up rate constant, and critical surfactant concentration are presented in Table 6 (104). Several other methods are being explored to improve the efficiency of ELMs in order to meet higher emulsion stability requirements. Recently, studies were conducted by Nii et al. (105) to demonstrate an ELM process using ferromagnetic particles in an operation mode. The objective of using W/O emulsion drops containing magnetic particles in a column operation is to provide possibility of unique drop motions, such as fluidization or vibration in the aqueous phase which are favourable for interface mass-transfer. Moreover, the phase separation of the emulsion from the continuous aqueous stream can be enhanced by magnetic force. Such advantages make up for the draw backs in the ELM processes, and they provide the potential for a column operation as well.

The performance of this technique was tested by the extraction of zinc(II) (10 ppm) from an aqueous stream at pH 3.4 by oil and W/O emulsion drops containing 0.1 M D2EHPA/dodecane in a spray column under magnetic fields. In this system, drop motion behaviour was also observed. The presence of ferromagnetic particles in the organic phase had no significant effect on extraction behaviour in the absence of magnetic force. For the W/O drops, more flexible operation was achieved by setting up permanent magnets to separate the dispersed phase from the continuous phase. When the alternating magnetic field is applied to the column in counterflow mode, magnetic W/O drops are held in the field and result in the formation of a

Table 6

Values of break-up rate constant (k_{bc}) and critical surfactant concentration (C_{sc}) for ELM

Surfactant	C_{sc} (mol/m^3)	k_{bc}(s^{-1})	Solvent	Extractant	C_{HR} (mol/m^3)
$2C_{10}GE$	5.0	1.6 10^{-6}	toluene	---	---
$2C_{12}GE$	4.2	9.7 10^{-7}	toluene	---	---
$2C_{14}GE$	4.0	1.8 10^{-6}	toluene	---	---
$2C_{16}GE$	3.2	4.5 10^{-6}	toluene	---	---
$2C_{18}GE$	3.1	1.7 10^{-5}	toluene	---	---
$2C_{18}\,\Delta^9GE$	2.0	9.2 10^{-7}	toluene	---	---
$2C_{12}QA$	35	1.9 10^{-5}	toluene	---	---
$2C_{14}QA$	17	2.4 10^{-6}	toluene	---	---
$2C_{16}QA$	7.0	1.3 10^{-6}	toluene	---	---
$2C_{16}QA$	4.3	1.3 10^{-6}	toluene	---	---
Span80	27	3.5 10^{-6}	toluene	---	---
Polyamine	31	2.0 10^{-6}	toluene	---	---
$2C_{18}\,\Delta^9GE$	2.7	1.0 10^{-6}	n-heptane	LIX65N	50
$2C_{18}QA$	4.7	1.6 10^{-5}	n-heptane	LIX65N	50
Span80	32	2.9 10^{-6}	n-heptane	LIX65N	50
Polyamine	35	1.4 10^{-6}	n-heptane	LIX65N	50
$2C_{18}GEC_2QA$-C_2PA	4.4	2.7 10^{-6}	n-heptane	LIX65N	50
$2C_{18}\Delta^9GEC_2$-QAC_2PA	5.3	1.1 10^{-6}	n-heptane	LIX65N	50
$2C_{18}\Delta^9GE$	5.0	3.5 10^{-7}	n-heptane	LIX65N	50
$2C_{18}\Delta^9GEC_2$-QAC_2PA	15	5.0 10^{-7}	n-heptane	PC88-A	50
Span80	40	4.0 10^{-7}	n-heptane	PC88-A	50
Polyamine	55	1.0 10^{-6}	n-heptane	PC88-A	50
Span80	15	2.5 10^{-6}	n-heptane	DDTPA	10
$2C_{18}\Delta^9GEC_2$-QAC_2PA	10	9.0 10^{-7}	n-heptane	DDTPA	10

Source: Ref. 104

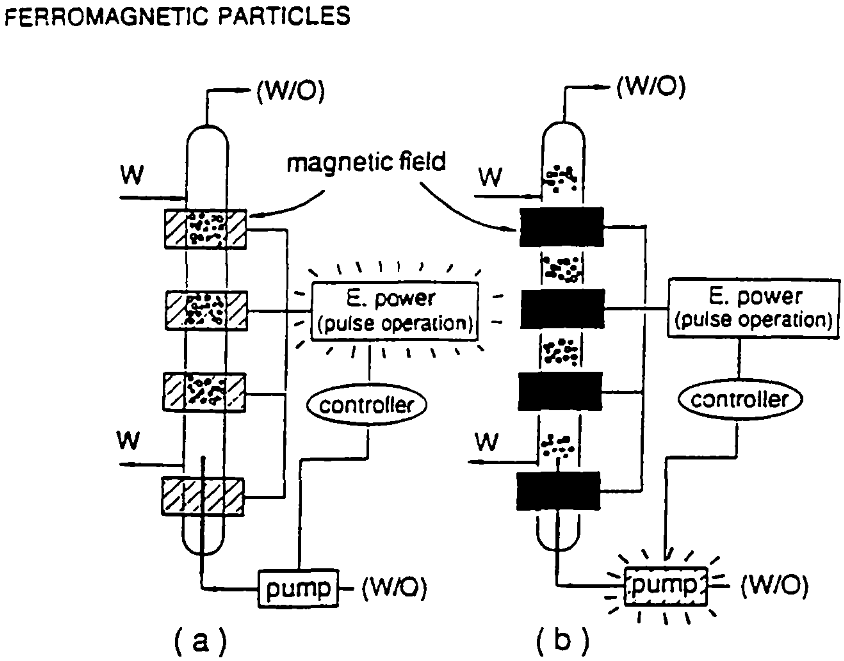

Fig. 13. Schematic diagram of sequential control of hybrid operation of a moving bed and spray column (a) current on (b) current off (reproduced with the permission of Marcel Dekker, Ref. 105).

fluid packed bed which provides an effective contact between phases. On the basis of their observation of drop behaviour, the authors propose hybrid operation of a moving bed and a spray column for ELMs containing magnetic particles in a cascade of alternating magnetic fields. The conceptual design of the hybrid operation mode is shown in Fig. 13a (when the current is on) and Fig. 13b (when the current is off). Similarly, Stevens and co-workers (106) and Yurtov et al. (107) focussed on the control of rheological properties of the organic membrane phase to obtain stable emulsions. Thus, in the design of the membrane phase there is a need to keep the solvent viscosity low to ensure that high mass transfer rates are maintained and to maximise the amount of dissolved polymer so as to increase the degree of elasticity and stabilise the emulsion. The membrane used in this investigation was composed of 0.2% polyisobutylene (PIB) supplied by Exxon (Vistanex MMI-140, MWT = 1.5 10^6) dissolved in 10% Shellsol 2046 (kerosene), and 89.8% HYVIS 3 (polybutene). The rheological properties of the stabilised membrane investigated are shown to be affected during the production of emulsion, possibly owing to the production of a fine stable dispersion of the internal phase in the membrane phase. These membranes have the advantage that emulsion stabilisation is controlled by temperature, and thus, forming and breaking the emulsion is an easily reversible process. Control of the drop size of the internal phase was reported to be very important in the overall performance of the process (106).

In most studies, commercial surfactants are used and there are very few studies concerning the development and design of a suitable surfactant for the separation of metals by ELMs (98, 108-110). In a recent work (110a), using calixarene derivatives as the carrier, extraction behaviour of rare earth metals (Ho(III), Er(III) and Y(III) from aqueous pH 5.3-5.6 was studied for ELMs using 2C18Δ^9GE as surfactants in toluene and 0.1 M sulphuric acid as an internal solution. The calixarene carbonyl derivative, namely *p*-tert-octylclphenoxyacetic acid, ^{t}Oct[4]CH_2COOH showed a high extractability for all rare earth metal ions. The use of aromatic diluents such as toluene, however, limits the further application of this study. In another study, the effects of synthesised surfactants on the extraction rate and separation of rare earths by ELMs were examined by Goto and associates (110b). The non-ionic surfactant $2C_{18}\Delta^9$GE and the cationic surfactant $2C_{18}\Delta^9GEC_2QA$ were used to form an emulsion with PC-88^a/n-heptane with 0.5 M H_2SO_4 as the internal phase. The extraction rate of lanthanides is found to be strongly affected by the structure of the hydrophilic part of a surfactant. Their extraction rate when using a cationic surfactant is faster than when using a non-ionic surfactant because of the interaction between the cationic surfactant and the anionic carrier (e.g., PC-88A) at the interface. It was found that the surfactant has a marked effect on the extraction rate and separation of lanthanides. A cationic surfactant accelerated the extraction rate of rare earth metals by ELMs and showed that separation of La(III) from Pa(III) and Nd(III) is feasible. The effects of surfactants on the extraction rate and separation of La(III), Pr(III) and Nd(III) are shown in Fig 14. Similarly, anionic surfactants accelerated the extraction rate of copper ions with a hydroxyoxime extractant, namely LIX 65N, as a carrier (109). The extraction rate of copper(II) ions with the amphoteric surfactant was about 50 times higher than with the non-ionic surfactant. However, the optimum surfactant concentration changes if a target material or composition of the membrane phase (carrier, solvent etc.) is changed.

Recently, the extraction and separation of platinum group metals (PGM) from chloride media by ELMs was reported by Nakashio and co-workers (111-115). Detailed studies of the extraction of Pd(II) by ELMs (emulsion prepared by extractant DDTPA using different surfactants: $2C_{18}\Delta^9$GE, $2C_{18}\Delta^9GEC_2QA$ and $2C_{18}\Delta^9GEC_2QAC_2PA$) were performed (111). The surfactant $2C_{18}\Delta^9GEC_2QAC_2PA$ was found to be most suitable from the viewpoint of both the permeation

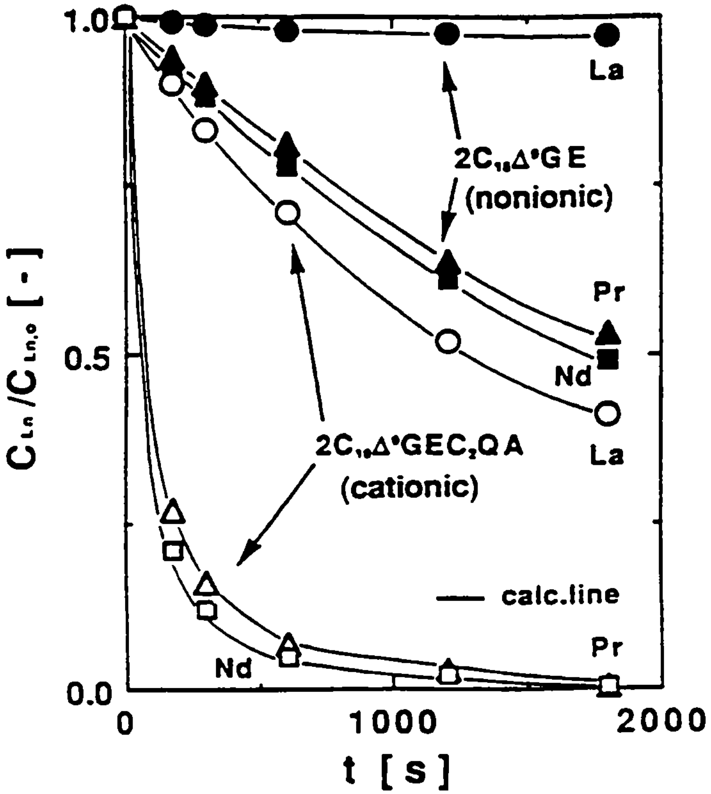

Fig. 14. Effect of surfactants on extraction rate and separation of La, Pr and Nd (C_{HR} = 0.05 mol m^{-3}),(pH = 2.0) (reproduced with the permission of American Chemical Society, Ref. 110b).

rate of Pd(II) and the stability of the ELM system. Emulsion stability increased with an increase in surfactant concentration, but the permeation rate of palladium decreased because the reaction interface was coated with the surfactant layer. The optimal concentration of surfactant was about 0.005 M for the efficient recovery of the palladium. Thiourea was used as the internal phase and its optimum concentration was 0.05 M. In subsequent studies, Kakoi and associates (112) performed the separation of palladium from waste water containing a large amount of iron by ELMs in a batchwise operation using dihexyl sulphide as carrier and acidic solution of thiourea as strippant. The separation factor of palladium with respect to iron using two different surfactants, namely Span 80 and $2C_{18}\Delta^9GEC_2QAC_2PA$, was 220 and 640 respectively, under optimum conditions. In the ELM system, the control of the thiourea permeation was reported to be a key factor and exact control of residence time was required in order to process the effluent on an industrial scale. In PGM separation, Goto et al. (113) proposed an ELM scheme using modified bifunctional surfactants which are able to act as both emulsifier and carrier. The bifunctional surfactants not only stabilised a water-in-oil (W/O) emulsion in a relatively low concentration but also showed high extraction ability for Pt(IV) from HCl solutions. In an ELM formulated with the bifunctional surfactants, Pt(IV) ions were selectively extracted from Pd(II) ions and concentrated rapidly from the aqueous feed solution to the inner receiving phase of W/O emulsions through a thin liquid membrane. As a counter ion for metal stripping, perchlorate ion could be employed and heptane was used as the diluent. The separation factors for Pt(IV) with respect to Pd(II) using surfactant/carrier $C_{18}/C_{18}\Delta^9QA$ and $2C_{18}\Delta^9QA$ were reported to be 10 and 11 respectively. In a similar study, Kakoi et al. (114) performed the recovery of Pd(II) from industrial waste water using di-2ethylhexyl monothiophosphoric acid (MSP-8) with an ELM system. Under the present optimum conditions of 0.01 M MSP-8 and Span 80, 0.1 M thiourea and 1 M HCl, more than 95% of the palladium was selectively recovered from the waste water in the presence of a large amount of iron, and was concentrated tenfold. Likewise, the recovery of palladium from nitric acid solution containing Ag(I) was accomplished by application of ELMs using the extractant LIX 860, a β hydroxy oxime, n-heptane as diluent and Span 80 as surfactant in a stirred tank (115). Sulphur containing extractants were shown to be non-selective mobile carriers in the separation process of Pd(II) and Ag(I) because they extract Ag(I) ions as well as Pd(II) ions. A chelating extractant, LIX 860, was found to be the most suitable extractant among those used. The internal solution used was 0.1 M thiourea and the external solution was Pd(II) and Ag(I) in 1 M HNO_3. Under optimum conditions, Pd(II) ions permeated preferentially as compared to silver ions through the thin liquid membrane phase and concentrated in the internal recovery phase.

Break-up rate of emulsion globules

To evaluate the stability of emulsion globules in a mixer, the break-up rate constant (s^{-1}), k_b, is defined by the equation (116)

$$\ln(1-\alpha) = k_b\, t$$

where t is time and α is the degree of break-up, which is obtained by the amount of break-up tracer released from the internal aqueous solutions of the emulsion globules into the external aqueous solution. The value of k_b decreases with an increase in the surfactant concentration, C_s, and the values k_b become a constant, k_{bc}, in the range of concentration higher than a critical value, C_s. That is, the stability of the emulsion increases with C_s in the range of surfactant concentration lower than C_{sc}, but its stability becomes constant in the range of concentration higher than C_{sc}.

The capability of the surfactant to stabilise the emulsion globules is expressed by the values k_{bc} and C_{sc}. A higher capability of the surfactant corresponds to lower values of k_{bc} and C_{sc}. These values are affected by the properties of the surfactant, the extractant and the organic solvent. It was found that the values of k_{bc} and C_{sc} are influenced by the alkyl chain length of the surfactant and that surfactants having two oleyl chains form more stable emulsion globules than do other surfactants having saturated alkyl chains, as shown in Table 6.

Swelling rate of emulsion globule

It is well known that the emulsion globules in a mixer swell by water permeation due to osmotic pressure between the internal and external aqueous solution. The swelling of emulsion globules in a mixer is represented by the increase of water content in the emulsion,

$$Y = (V_{wi}/V_{wi}^{0}),$$

where V_{wi}^{0} is the initial content of water in the emulsion (117).

The swelling rate of the emulsion prepared by Span 80 is very high in comparison with the emulsions of other surfactants. In the initial period, i.e., in the first few minutes, the effect of swelling is not too great, except for the emulsion of Span 80.

The permeation rate of water through the organic phase of the ELM increases with the difference of water activities in the external aqueous solutions and also depends on the properties and concentration of surfactant and extractant (104). However, swelling of the emulsion is an undesirable and avoidable phenomenon. Therefore, it is required that the rate of metal extraction by the ELM be raised sufficiently so that the separation of metal by the ELM in a mixer is completed in a few minutes.

Advances in de-emulsification technique

In the process of liquid membrane separation, de-emulsification and the reuse of the oil phase is necessary for continuous separation (118). De-emulsification is the final step of the ELM process, where the enriched internal aqueous phase and the organic phase must be recovered and where the organic phase is repeatedly recycled. In the ELM process, breaking of the loaded emulsion is one of the key steps. The most efficient and economic method for breaking (W/O) emulsion in the ELM technique is to apply an electrostatic field. Electrostatic coalescence is a technique widely used to separate dispersed aqueous droplets from oil (119). The effect of several operational factors on the emulsification rate was investigated, using various electrical coalescèrs (120-123). The mechanism of electrostatic de-emulsification is not fully understood

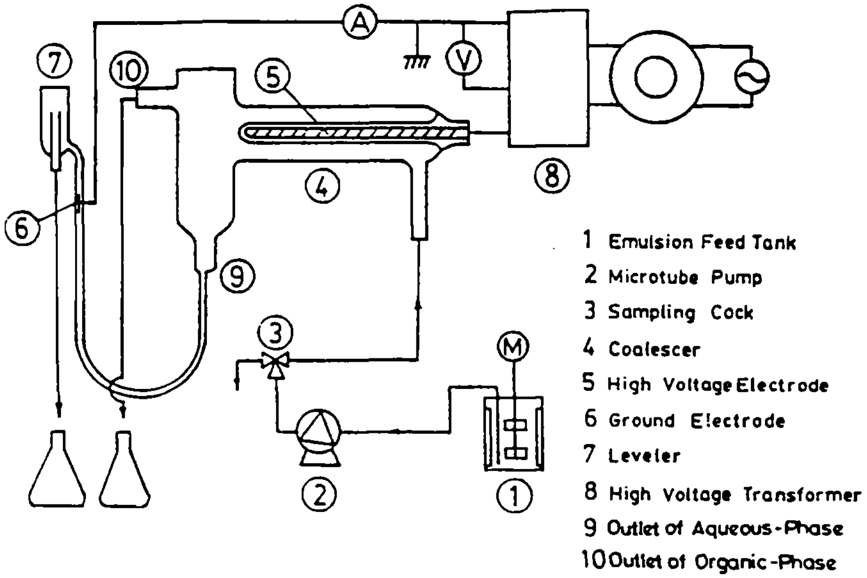

Fig. 15. Continuous tubular electrical coalescer for de-emulsification of W/O emulsion (reproduced with the permission of the Society of Chemical Engineers, Japan, Ref. 104).

(108, 124). According to the theory of emulsion coagulation (118), emulsion break-up is a three-step process. In the first step, called flocculation, the dispersed droplets of the internal phase flocculate into large groups but drops still exist without coalescence. In the next step, coalescence, the drops in groups coalesce into a large drop resulting in a decrease in the number of drops. Finally, in the sink step, large internal drops sink by gravity to the interface between the oil and the water and coagulate into the water phase, resulting in the break-up of the emulsion. All three effects are influenced by the electric field. The general understanding is that the electric field can polarise and elongate water droplets. The neighbouring water droplets, after acquiring induced charge from the electric field, will attack each other and coalesce into a large drop.

In the continuous tubular electrical coalescer shown in Fig. 15, the de-emulsification rate constant, k_D, is defined by the following equation (100):

$$-(d\phi_w/dx) = k_D\theta\phi_w{}^n$$

where ϕ_w is the water content in the emulsion, x is a dimensionless distance from the inlet of the tubular coalescer, θ is the mean residence time of the emulsion in the coalescer, and n = -1.

Recently, the mechanism of electric de-emulsification and the coalescence behaviour of the internal water drops in oil under the influence of an electric field were described by Gang et al. (118). They proposed a new concept of critical electric field intensity of emulsion. They discussed the effect of several parameters such as internal drop diameter of the emulsion, surfactant concentration, applied voltage, electric field frequency, effect of temperature and aging time of emulsion. It is reported by the authors that de-emulsification is a three-step process which can be accelerated with the aid of an electric field. When the applied electric field intensity is higher than the critical electric field intensity of the emulsion, the de-emulsification rate is controlled by the flocculation rate of emulsion, otherwise the emulsion cannot be broken. Their concept of critical electric field intensity could well serve to provide a satisfactory explanation of some of the experimental phenomena. The proposed equation is shown below:

$t_b = \mu(d_r^3 - d_p^3)/(K_1 \phi T + K_2 \phi E^2 f)$

From the equation, it can be seen that applied voltage (E), frequency of electric field (f), diameter of initial water drop (d_p), volume fraction of water phase in emulsion (ϕ), temperature (T) and viscosity of the emulsion (μ) are the main factors which affect the de-emulsification rate. In a very recent study (122), Draxler et al. used computational fluid dynamics software to evaluate the preparation of the emulsion and various improved devices for splitting it. In the case of electrostatic splitting of emulsion, they propose combining the fluid flow pattern with the electric forces acting on the droplets. The authors claimed generally satisfactory performance of the homogeniser device although there were some limited drawbacks.

Electrostatic pseudo liquid membrane

Recently, a new concept of liquid membranes was introduced by Gu (125), who combined an electrostatic field with the principle of the liquid membrane and developed a new type of separation method which they named electrostatic pseudo liquid membrane (ESPLIM). A reaction tank is filled with the extractant and diluent, and it is divided into an extraction cell and a stripping cell by a perforated plate. The organic solution can flow through the perforated plate while the added feed and stripping aqueous solutions on both sides of the plate are completely separated. There are settlers for the aqueous solution below the extraction cell and the stripping cell. These two settlers are separated by a partition. When an alternating current (ac) high-voltage electrostatic field is applied simultaneously to both cells, the feed and stripping solution added to the extraction and stripping cell respectively are dispersed into numerous droplets in the continuous organic phase. The complex formed in the extraction cell diffuses through the baffle plate into the stripping cell, where the product is released.

Table 7

Typical experimental conditions and results for the extraction of cobalt from aqueous solutions

Process Conditions	
Feed	1000 ppm Co^{2+}, 0.1 M sodium acetate, pH = 5
Stripping solution	1 M H_2SO_4
Oil phase	Kerosene containing 10% (v/v) D2EPHA
Operational conditions	
Voltage	3.0 kV
Current	670 μA
Flow rate of feed	$2\ 10^{-4}\ m^3/h$
Flow rate of stripping solution	$1\ 10^{-5}\ m^3/h$
Mean residence time of aqueous droplets in electric field	4 s
Results	
Co^{2+} concentration in raffinate	10 ppm
Co^{2+} concentration in stripping solution	19,750 ppm
Concentration of cobalt complex	300 ppm (in stripping cell)
pH in raffinate	4

Source: Ref. 126

ESPLIM offers the same advantages as liquid membrane separation systems, such as higher rate of mass transfer, fewer separation stages and lower extractant inventory. Furthermore, this technique, standardised by Gu (125), affords a flux (10^{-7} mol/cm^2/s) which is one order of magnitude higher than that of SLMs. He showed that about 99% extraction of Co(II) could be readily achieved after the aqueous droplets containing 1000 ppm Co(II) merely passed through a 100 mm high electrostatic field with a duration of only 4 seconds by means of a small rectangular set-up, which was about 12 cm high, 8cm wide, and 1.5 cm thick. The Co(II) concentration increased to 20,000 ppm in the stripping phase. The consumption of electrical power was only 2 watts. The typical results of cobalt extraction through ESPLIM are summarised in Table 7 (126). Similarly, good results were obtained with Eu(III), reaching 95% extraction using P 5709 (a phosphonic acid-type extractant synthesised by the Beijing Institute of Uranium Ore Processing) using a similar set-up with an enrichment factor of 60 in the stripping phase. The residence time of aqueous droplets in the electric field was approximately 4 seconds (127). Subsequently, recovery of Y(III) by P 507 (dialkyl phosphonic acid extractant) was found to be very efficient. In this study, a ESPLIM reaction tank composed of a number of two-cell units in parallel was used. Its out side dimension was 20 cm high, 40 cm wide and 55 cm long, with a treatment capacity of 30-45 l/h. A stereogram of multicell reaction tank is shown in Fig. 16(a). Fig. 16(b) shows the flowsheet for Y(III) extraction by ESPLIM. By partially circulating the stripping solution, Y(III) could be concentrated from 1.0 to 232 g/L with one step operation. The impurities such as La(III) and Ca(II) were poorly extracted during the process which resulted in Y(III) purification from 94.3 to 99.7 % (128). Using a similar set-up, separation of scandium was performed from rare earths by Gu and co-workers and recovery was reported to be more than 95% (129).

ESPLIM mechanism

The vertical counter-current extraction and stripping processes taking place in the extraction and stripping cells respectively, together with the lateral transport process of the complex and the extractant across the two cells, constitute the ESPLIM process. By combining the vertical and lateral mass transfer processes, the following fundamental equations are obtained:

Extraction side: $-\frac{dx}{dh} = \frac{K_w a S}{Q}(x - x_i)$,

Stripping side: $\frac{dZ}{dh} = \frac{K'_w\ a'\ S'}{Q'}(z_i - z)$,

It must be borne in mind that the above equations solely describe the ideal situation in which no backmixing is considered. The permeation constant of solute through the baffle plate P and mass transfer flux can be expressed as follows (125):

$$P = \frac{Q(x_f - x_p)}{\lambda A(y_e - y_s)_m}$$

$$J = 10^{-3}\frac{Q(x_f - x_p)}{\lambda A}$$

As compared to all other LM techniques, ESPLIM has its own limitations. It is only effective when the continuous phase is an organic solution of low polarity and the dispersed phase is an aqueous solution. It is confined to the extraction and separation of solutes from aqueous solutions. To overcome high voltage difficulties, some other methods such as spray or ultrasonic technique could be an alternative to the electrical field to achieve phase dispersion. Zhou and Gu

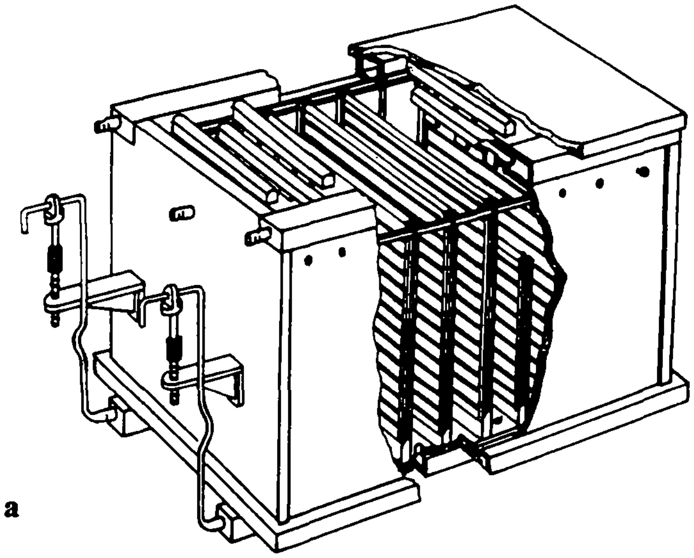

Fig. 16(a). Stereogram of multicell reaction tank of ESPLIM (see text for more details) (reproduced with the permission of Elsevier Science, Ref. 128).

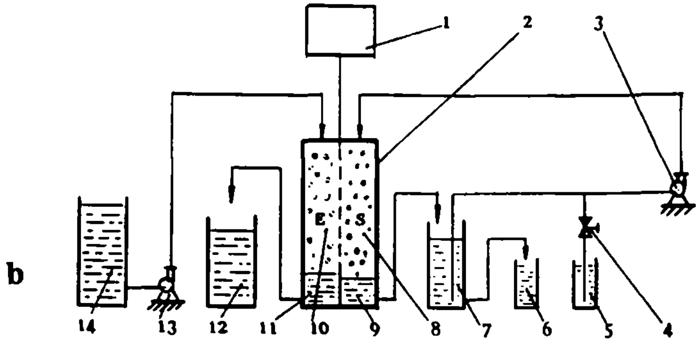

Fig. 16(b) Schematic flow sheet of continuous extraction of Y(III) by ESPLIM. (1) H.V. power supply; (2) reaction tank; (3) reflux pump; (4) adjusting valve; (5) HCl Tank; (6) concentrate receiver; , (7) reflux tank; (8) stripping cell; (9) stripping settler; ; (10)extraction cell; (11) extraction settler; (12) raffinate tank; (13)pump; (14) feed (reproduced with the permission of Elsevier Science, Ref. 128).

(127, 130) studied Co(II) extraction using a spray pseudo liquid membrane set up with D2EHPA as the carrier. The feed solution contained 1000 ppm cobalt(II) and 0.1 M CH_3COONa with an initial pH of 5, and the stripping solution was 2 M H_2SO_4. The concentration of organic carrier (D2EHPA) was 15% (v/v) in kerosene. The extraction rate was well above 98% when flow rates of feed and stripping solution were maintained at 125 and 28 ml/h respectively. Using the same set-up as mentioned above, the authors reported the permeation of Eu(III) as around 74.6% from 3 M HNO_3 by a neutral bidentate organophosphorous extractant, namely diethyl carbamoyl methylene phosphonate (DMDECMP). The recovery or removal of tri, tetra and hexavalent actinides including Am(III) from certain highly acidic nuclear fuel cycle waste steams could be possible using this technique. It is very important to remove long-living actinides from reprocessing waste, given the potential hazard of storing these nuclides together for a period of years.

In the ESPLIM process, leakage refers to the leak of the stripping solution from the stripping cell to the extraction cell during operation. The leakage rate varies as a function of baffle structure, applied voltage, etc. Gu (131) reported that the maximum leakage rate under these experimental conditions was 0.06%, which was much lower than any value reported in ELM processes. The concept of "swelling" is regarded differently in ESPLIM techniques. In ESPLIM, feed droplets could be entrained by the oil solution (continuous phase) from the extraction cell through the baffle channels to the stripping cell. This entrainment is regarded as "swelling" by analogy with that in the ELM process. Here, the swelling rate is defined as the volume ratio of the entrained feed solution per unit time to the flow rate of stripping solution. The author has claimed that by properly adjusting the baffle structure and the operational conditions, the swelling rate could be controlled to ≈ 1%.

The same configuration of spray pseudo liquid membrane has been studied under another name as emulsion free liquid membrane (EFLM). Its applicability was tested for treatment of low and medium level radioactive wastes by Shukla et al. (43a) and removal of heavy metals from waste streams by Kumar et al. (132). This technique was applied in decontamination of U(VI) from a simulated reprocessing waste through a TBP liquid membrane. The feed and the strippant were passed through the carrier in a jet of very fine droplets by mixing these liquids with compressed air. EFLMs retain the major advantages of LMs, such as high flux, high selectivity and low consumption of reagents, and overcome some of the shortcomings of other LMs, such as the poor permeant diffusion rates, the high swelling of ELMs and the instability of SLMs. TBP, a commercial extractant, was used as a uranium complexing carrier. Feed acidity was maintained at 2 M HNO_3 and 1 M Na_2CO_3 was most successful as the strippant. With U(VI) concentration

Table 8

Experimental details and results of uranium transport across the EFLM

[Feed]	2 mmol dm^{-3} U in 2 M HNO_3
[Strippant]	1 M Na_2CO_3
[Carrier]	30% TBP in dodecane
Flow rate of feed and strip	1000 ml/h
Results	
[Uranium] in raffinate	0.2 mmol dm^{-3}
[Uranium] in stripping solution	1.81 mmol dm^{-3}
[Uranium] in membrane phase	0.017 mmol dm^{-3}
Uranium transport	90.5%

Source: Ref. 133

of 2 g dm^{-3} in 2 M HNO_3, the recovery was well above 90%, a flow rate of nearly 1 l/h being maintained under the optimal recovery conditions. Some interesting results of U(VI) pertraction across EFLMs are presented in Table 8 (133). Similarly, the permeation of heavy metals such as Cu(II) and Cr(VI) was performed employing EFLMs (132) using LIX 64 (10% v/v) and Alamine 336 (2% v/v) in kerosene, and the recovery of copper and chromium was found to be more than 95% into a product phase consisting of the strippant $NaOH/Na_2CO_3$. The authors claim the effectiveness of the separation technique, but a highly hydrophobic extractant and diluent are needed in order to prevent the contamination of aqueous stream with traces of extractant/diluent.

Reverse micelle or Microemulsion

Recently, a reversed micelle system which is similar to the LM system has attracted much attention as a new separation technique. The emulsions described under ELM section are formulated by inputting mechanical energy and over a period of time can separate, partly or wholly, into their constituent phases. Hence, a new concept of reverse micelle or microemulsion, which overcomes these shortcoming of macroemulsions, was introduced (20). A microemulsion forms spontaneously when the aqueous and organic phases are brought in contact in the presence of a surfactant (as well as co-surfactants in many cases). Because it is in thermodynamic equilibrium, microemulsion systems are very stable. In addition, they are optically transparent, and can display a wide range of water volumes - from completely water-continuous to completely oil-continuous in structure. Though the physical nature of the microemulsions is quite different, they exhibit an identical mechanism of liquid membrane separation. The size of the microemulsion droplet is in the range of 0.005 to 0.1 μm as compared to a typical macroemulsion droplet measuring 1μm. The much larger surface area provided per unit volume for internal droplets in the microemulsion system is ultimately responsible for the rapid extraction rates. Microemulsions also have characteristics such that the corresponding operation of de-emulsification can be easily carried out by employing an organic solution containing reversed micelles with an aqueous stripping solution and adjusting the pH and the concentration of a salt.

Microemulsions, because of their higher stability, offer potential advantages when used as liquid membranes over emulsion liquid membranes. Thus, a technique involving reversed micelles or microemulsion instead of macroemulsion droplets is proposed by Harada et al. (134). They conducted the separation of metal ions using reversed micelles formed by di-2-ethylhexyl sulphosuccinate sodium salt (commercial abbreviation AOT) and reported that metal ions could be concentrated by an LM process using microemulsions. Similarly, the transport of Ni^{2+} ions by two microemulsion systems was studied by Tondre et al. (135a). The first system was tetraethylene glycol dodecyl ether ($C_{12}EO_4$)/1-hexanol/n-decane/water and the second system was AOT/n-decane/water (0.25M salt). They concluded that loading and unloading of microemulsion droplets with substances to be transferred through liquid-liquid interfaces does not obey a general mechanism. Depending on the nature of the surfactant involved, either "direct" (system II) or "indirect" (system I) interfacial loading /unloading could take place. Like wise, transport of potassium and sodium picrates was measured by Xenakis et al. (135b) in presence of two mobile carriers : water-in-oil microemulsion droplets and lipophilic crown ethers. A lower flux was observed when the microemulsion droplet and crown ether could diffuse as a single entity. On the other hand, larger synergistic effects could be observed when extractant could diffuse independently of the microemulsion droplet. Hence, if microemulsions are used as transfer agents in conjugation with selective extractants to improve the transfer rate of metal ions, it would be advantageous to choose a lipophilic extractant that is soluble in the continuous organic phase rather than interating strongly with the microdroplets constituting the dispersed phase. Similarly, Tondre et al. (135c) carried out the complexation of Ni^{2+} with two extracants namely 8-hydroxyquinoline (HQ) and 7-(4-ethyl-1methyloctyl)-8-hydroquniline (C_{11}-HQ) in presence of microemulsions to study the kinetics and mechanism of reactions that usually take place in highly heterogeneous conditions. Their objective of this work was to show that microemulsions could be employed to improve the understanding of the complicated reactions taking place in liquid-liquid extraction process. On similar line, Kim et al. also demonstrated that microemulsions of lipophilic extractant could be chosen to slow down the rates of complexation of Ni(II) and Co(II). This was possible by taking advantage of the electrostatic repulsions between the metal ions and the charged surface of the dispersed particles.

The overall efficacy of microemulsion based extraction of Cu(II) from water by incorporating benzoylacetone (136a) and Hg(II) from water by incorporating oleic acid (20b, 136b), was reported. The expected benefits of the LM process were evident in that concentration of mercury in feed water was typically lower when using microemulsions than when using macroemulsions (136a) . Model simulation showed the expected effects of pH and equilibrium constants on extraction kinetics and interior concentration profiles. The model could predict both the initial extraction kinetics and final mercury extraction equilibrium. The agreement between the theory and experiment suggested that the mechanism of extraction using microemulsion is very similar to that of macroemulsion once the appropriate physical parameters which distinguish microemulsion from macroemulsions have been incorporated. The recovery of Hg(II) from microemulsion was accomplished by de-emulsification. The macroemulsions were de-emulsified by an electrostatic technique, while addition of co-solvent was required for the microemulsions (137). After treatment of the organic phase by distillation (butanol removal), the microemulsion was formed and utilised again to separate Hg(II) from the feed phase. The system was not as efficient as the fresh microemulsion system. The lowered efficiency was directly related to the use of a co-solvent in the de-emulsification step. Although most of this co-solvent was distilled out of the solvent before its reuse, the small residual content of butanol generally increased the leakage in the system, which ultimately resulted in reduced separation efficiency. The addition of a co-solvent is undesirable because it introduces another step for co-solvent separation. In the light of this, macroemulsions are to be preferred to microemulsions.

Hybrid techniques

Emulsion liquid membranes utilising hollow fibre contactors

To extract and strip the metal ions simultaneously from waste water, an ELM can be coupled with a liquid-liquid dispersion-free hollow fibre contactor (HFC). This combines the advantages of ELM separation (simultaneous extraction and stripping) and dispersion-free solvent extraction. The leakage of the internal stripping phase to the feed is minimised in the absence of high shear rates, as occurs in stirred contactors (SC). The internal droplets are generally larger than the typical pore size of the membranes and do not come into contact with the aqueous feed stream. The tendency to swell is thereby reduced. Fig. 17 represents a scheme of ELM

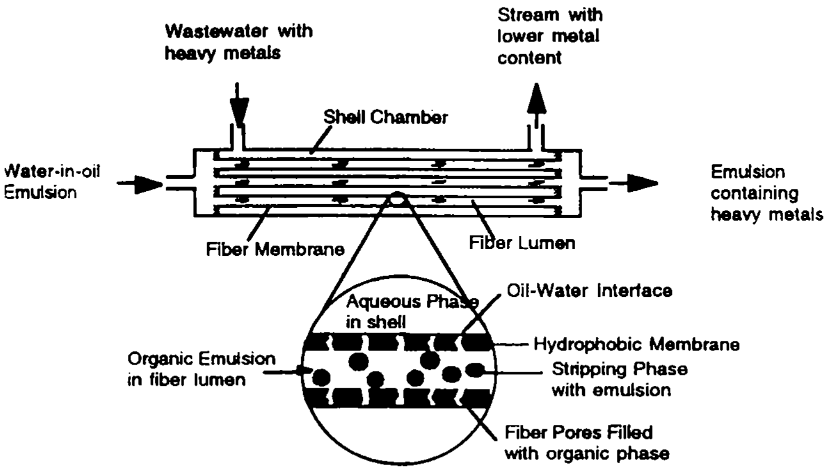

Fig. 17. Hollow fibre contactor used for emulsion liquid membrane studies (reproduced with the permission of American Institute of Chemical Engineers, Ref. 138).

extraction in a hydrophobic HFC. Raghuraman et al. (138) have described the merits of ELMs in HFC. The permeation fluxes were comparable to a traditional stirred contactor system. Overall rates were slower owing to the smaller area on lab scale of the membrane module. On the other hand, owing to low swelling and leakage, separation efficiency is higher. The swelling was observed between 0-20% whereas in the SC it was in the range of 80-100%. In HFC, there was no detectable leakage of the internal phase into the feed. Fig. 18 compares extraction of Cu(II) in the two contactors when the emulsion is stabilised with 3 wt% surfactant. It was possible to attain ppb levels of residual Cu(II) using HFM contactor without displaying any leakage. The emulsion stability was not considered an important factor in the HFC. Using HFC, copper could be removed to a level one order of magnitude lower than in an SC. The authors' opinion is that there would be an added advantage when using less stable emulsions in the contactors. The emulsion, by lowering the surfactant concentration (even as far as 0%) in the emulsion of an ELM, afforded a comparable performance to that of an HFC without any loss of extraction efficiency. This suggests the possibility of eliminating the downstream de-emulsification process.

Liquid membrane film pertractors

In order to improve stability aspects of LMs, some authors have developed new liquid membrane configurations. What they all have in common is a combination of the bulk liquid

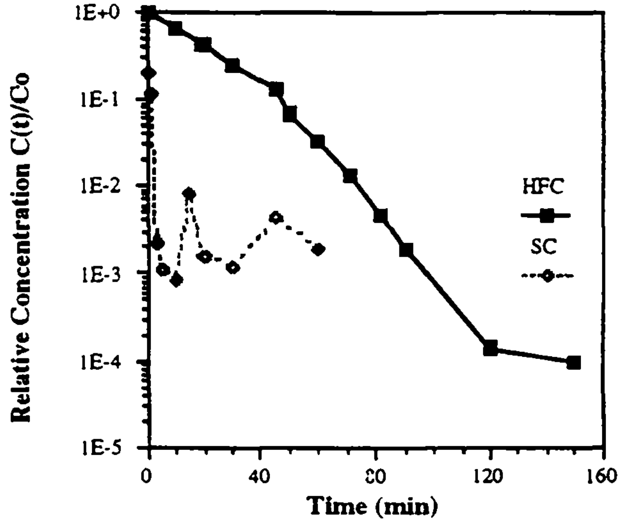

Fig. 18. Comparison of extraction of copper(II) in a stirred contactor (SC) and hollow fibre contactor under similar chemical conditions, Cu(II): 1000 ppm at pH 5.36, Emulsion: 3 wt% CA5025 as surfactant and 5wt% LIX 84 as extractant, Internal phase: 18 wt% 6N H_2SO_4, diluent: n-tetradecane, Stirring speed in SC: 400 rpm, Flow rate of aqueous phase in HFC: 40 ml/min and emulsion stationary phase in tube, Ratio of aqueous phase to emulsion 10:1 (reproduced with the permission of American Institute of Chemical Engineers, Ref. 138).

membrane and the supported liquid membrane. One component in the membrane phase is a carrier which selectively complexes with metal ion from the source phase and further permeates to the receiving phase, which has a strippant. It is claimed by several authors that this configuration is more promising as far as performance and stability are concerned.

The creeping film pertractor and rotating film pertractor were developed by Boyadzhiev and co-workers (10, 139-143) and also by Schlosser et al. (144). In contrast to the SLM and ELM techniques, all three liquids in liquid film pertraction (LFP) are in motion. In the creeping film pertractor, the feed and the stripping solution flow down the vertical solid porous supports, which are arranged in an alternating sequence with narrow spaces in between.

The rotating film pertractor, as well as the whole pertractor volume, is filled by the intermediate organic phase, which circulates in a co-current or counter-current mode, driven by an external pump or some other motion generator. Since all three liquids are in motion, the transfer of species is controlled by eddy diffusion, increasing all mass fluxes considerably. Although the real thickness of the vertical liquid "membranes" is in the range of several millimetres, they are (with respect to their mass transfer resistance) equivalent to completely stagnant liquid film only a few microns thick. Boyadzhiev et al. (10) conducted experiments on liquid film pertraction by using a laboratory type pertractor with a maximum capacity of 100 l/day (with respect to the feed) having an effective membrane area of 0.12 m^2 at the feed-membrane interface. Using this module, an attempt was made to remove Zn(II) from zinc-containing waste water using normal paraffins (C_{11} -C_{13}) containing 2 vol% of di-2-ethylhexylphosphoric acid as the membrane phase. The pertraction efficiency was claimed to be 99.8%. Similarly, in the experiments conducted to remove Cu(II), the pertraction efficiency was 99.6% for feed containing 0.25 g/l Cu(II) and finally as little as 1 ppm remained in the feed phase. A 1% solution of the commercial aldoxime ACORGA P-500 in the same paraffinic oil is the formulation of the organic membrane, and is later stripped by a 15% solution of H_2SO_4. This study demonstrated the selective separation of Cu(II) over Fe(III), Mg(II), Ca(II), Co(II) and Ni(II). Continuous operation times of more than 3000 h have been reported by Boyadziev without any efficiency loss or process deterioration. A liquid membrane technique for preconcentration of trace components from aqueous solution was reported by Lazarova et al. (142). Experiments were conducted to preconcentrate Cu(II) ions using a liquid membrane of C_{11}-C_{13} normal paraffins containing the commercial chelating extractant LIX 65N. Enrichment factors in the range of 5-15 were obtained using this technique.

In the rotating film pertractor, hydrophilic disks were mounted on a horizontal shaft. The lower parts of the disks were dipped in compartments alternately filled with stripping and feed solutions. The films of water were formed on the disks owing to rotation and these were immersed in the membrane phase where extraction and stripping took place. Boyadzhiev et al. claimed that the rotating film pertractor concept offered a stable operation without side effects under both continuous and batch experiments (10). A possibility has been reported (141) for direct treatment of leachates or mine waters containing Cu(II), producing conditioned cathode solutions for Cu(II) electrowinning. However, more experimental proof and evidence of economic feasibility is needed to determine the right place for this challenging new unit operation. The stability of these units and long term operationality and reproducibility need to be checked in order to gauge feasibility on an industrial scale. Likewise, recovery of Cu(II) from dilute ammonia leach solutions was performed using a rotating film pertractor employing LIX 54 (40% β- hydroxyoxime in kerosene) and H_2SO_4 as the stripping liquor (143). The authors established that the copper extraction step was controlled predominantly by the rate of copper ion mass transfer and the stripping step depended on the rate of copper-complex decomposition in the stripping side reaction layer. In recent studies, a mathematical model for recovery of Ag(I) from dilute nitrate solutions using the rotating film membrane technique was proposed by Boyadzhiev and co-workers (144). The membrane solution of 0.06 M of tri-isobutylphosphine sulphide (TIBPS) in n-octane and stripping reagent ammonia was used in order to achieve effective recovery of Ag(I). The modelling of the mass transfer revealed that stripping was a slower step, although the reaction between the silver-TIBPS complex and ammonia was instantaneous. A dynamic simulator, namely TUTSIM (Meerman Automation), was used to calculate the mass transfer coefficient, and its values in the aqueous films are nearly 10 times higher than the membrane side coefficients. Owing to the very high partition coefficient of the silver-TIBPS complex (distribution coefficient of silver complex, 1.45 10^6), mass transfer through the aqueous film was actually the rate controlling step during extraction.

Similarly, BLMs with porous partition membranes were used by Nii et al. (32). In this operation, feed and recovery sides were partitioned by a hydrophobic porous membrane, and a membrane solution was forced to flow with the feed or recovery solution within each flow channel. The membrane solution moves through the pores of the porous membrane freely, and the solute extracted within the feed side channel is transferred across the partition membrane by bulk motion of the membrane solution as well as by diffusion, i.e., the organic phase acts as a bulk liquid membrane. In testing such membrane modules, the feed solution was an aqueous solution of I_2-KI (I_3^-), the membrane solution was n-heptane and the stripping reagent was $Na_2S_2O_3$. Iodine in the membrane solution was extracted by the membrane solution and was transferred from the feed side to the recovery side across the porous membrane and was then stripped from the membrane solution. The feed and strippant solution were mixed with membrane solution and flowed upwards in their respective channels. Further, the aqueous and organic phases were separated from each other by a phase separator. In these experiments, it was shown that the operation has potential for rapid separation and concentration in comparison with SLM operations. In their operation, it was possible to obtain a large interfacial area between aqueous and organic phases by decreasing the channel depth and inserting a hydrophobic mesh spacer. Although a relatively large amount of membrane solution is needed for the operation in comparison with SLMs, this method can only be used with highly hydrophobic organic solution having very low aqueous solubility. If the membrane solution has high aqueous solubility then another secondary method has to be adopted for the removal of organic solution from aqueous streams. If the solvating type of extractants are used then pre-equilibration of the membrane solution with aqueous solution would help in achieving improved performance of such a liquid membrane configuration (145).

Hybrid liquid membranes (HLMs)

This system is intended to combine the selectivity of liquid membranes with the stability of ion-exchange membranes by preserving the exchange-diffusion mechanism of transport in the system components. To some degree, a multimembrane hybrid system coincides with the idea of an extraction process as realised by coupling an ion-exchange polymer membrane with a liquid organic extractant. The method was patented by Ho et al. (146) in 1976 and renewed recently by Kedem et al. (93). A system composed of an LM containing LIX 64N as carrier and several different ion-exchange membranes was employed for transporting Cu(II) ions. The main advantage of the multimembrane hybrid system reported by Wodzki (147) is the possibility of avoiding some problems caused by the instability of organic liquid membranes in contact with aqueous solutions. Donan exclusion of the ionic forms of an extractant and the high tortuosity of diffusion pathways are supposed to be practical ways to suppress the permeation of a carrier from an LM to feed and stripping solutions. Moreover, the ability of ion-exchange membranes to take up cations (or anions, depending on the charge of the ionogenic groups) from dilute solutions should result in high accumulation of reacting species at interfaces, thus probably enhancing the overall transport process. In the same context, the multimembrane hybrid system was developed by Wodzki and co-workers and used for the transportation and separation of divalent metal ions from multicomponent solutions. The system consists of three membranes in series:

ion-exchange membrane | liquid membrane | ion exchange membrane

The experiments were performed with liquid membranes composed of DEHPA in kerosene and Nafion-120 perfluorosulphonic acid polymer membranes. The fluxes and separation characteristics were determined for a multimembrane hybrid system separating a solution of Zn(II), Mn(II), Cu(II), Co(II), and Ni(II) sulphates as the feed phase, and the stripping phase containing sulphuric acid. The schematic representation of the transport mechanism in a multimembrane hybrid system is shown in Fig. 19. The selectivity order was reported in this system as: Zn(II)>Mn(II)> Cu(II) >> Co(II), Ni(II) and high separation factors were claimed for Zn(II), Cu(II) and Mn(II) as compared to Co(II) and Ni(II). In spite of the performance potential of the multimembrane hybrid system, very few papers have appeared on this subject in recent years. The main limitations of this type of system are the fabrication of the membrane modules and the complicated set-up. The permeability coefficients using ion-exchange membranes are reported to be of a low order of magnitude as compared to a liquid membrane (33). Therefore it would seem to be difficult to achieve better transport with an ion-exhange membrane.

The recent HLM technique was developed by Eyal et al. (16, 17). The constitution of an HLM

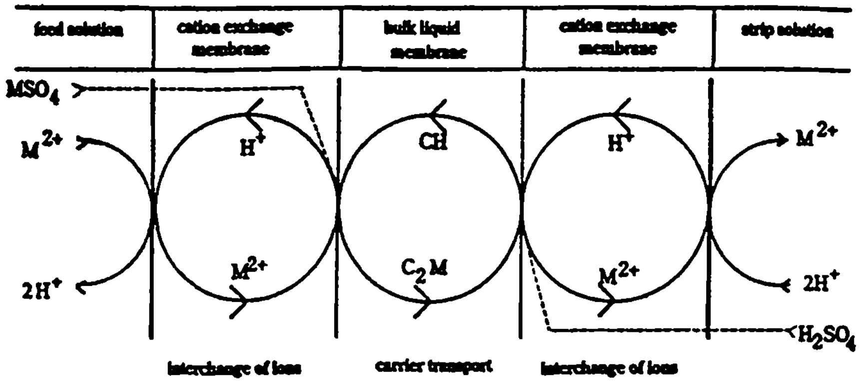

Fig. 19. Schematic representation of the transport mechanism in a multimembrane hybrid system (reproduced with the permission of Marcel Dekker, Ref. 147).

cell is shown in Fig. 20. It utilises an extracting reagent solution (carrier solution), flowing between membranes. The membranes, which separate the carrier solution from the feed and receiving solutions, enable the transport of solutes but block the transfer of the carrier to the feed or to the strip. The carrier is blocked by means of the membrane's hydrophilic/hydrophobic or ion-exchange properties, or its retention abilities, owing to pore size.

A theoretical model was developed by the authors for Ti(IV) transport through DEHPA in benzene as a carrier solution, from the feed to the stripping hydrochloric aqueous solutions. A close correlation between experimental and simulated data was observed. The HLM module should be operated in such a way as to achieve maximum mass transfer rate, i.e., by increasing the strip side interfacial area and decreasing the strip boundary layer resistance at a given total (feed and strip) membrane area. The HLM system is claimed to be similar to the HFCLM developed by Sirkar and co-workers (12, 14), with the exception of the flowing (or circulating) membrane (carrier) solution. The results for HLMs were compared with those for SLMs using titanium (IV) transport from low (pH = 0.65) and high 7 M HCl acidity feed with DEHPA in benzene, impregnated into Celgard-2400 membrane support, and fluxes ranging between 3-4 10^{-6} mol/m^2/s were observed. The rate-controlling step of the transport is the kinetics of the back extraction process. Similarly, Mohammed et al. (148) performed the LM study of Au(III) using dodecylthiourea and nonylthiourea in chloroform with a cell composed of three compartments, including a reservoir of organic solution, with double solid supported liquid membranes. The performance of the module was claimed to be satisfactory in terms of metal transport and membrane stability.

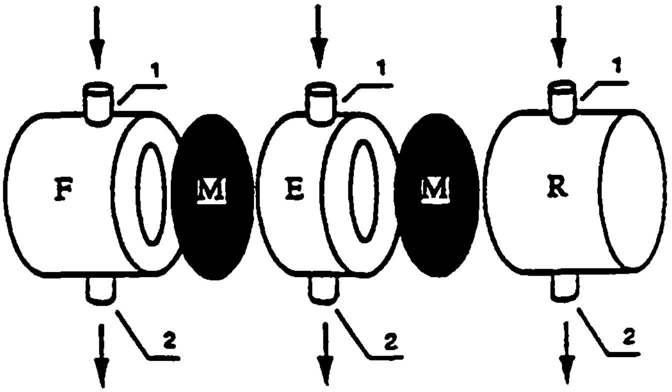

Fig. 20. Schematic diagram of the HLM system: F, E and R, compartments of the feed, membrane (carrier) and receiving solutions respectively; M, membranes; 1 and 2, inlet and outlet of the feed, carrier and stripping solutions. Gaskets, made of Vytone, were inserted between compartments and membranes (reproduced with the permission of Elsevier Science, Ref. 16).

In general terms, this study was similar to the studies conducted by Eyal (16, 17) except for the pressure across the reservoir, which established the organic interface in the pore of the membrane support.

Facilitated transport in solid state membranes

Working on several ways to improve liquid membranes, Guizard and associates (149-150) proposed a system of organic-inorganic membranes which are based on the incorporation of specific complexants into the dense solid membrane in order to increase the selectivity and permeability of specific metal ions. Different types of complexing agents have been chemically grafted onto polymeric membranes for facilitated transport applications and employed mainly for gas separations, which are not within the scope of this review. Flyes et al. (151) patented polymer membranes with grafted crown-ethers as carriers. They exhibit proton driven cation transport with selectivity typical of the crown ether moiety, indicating that its macrocyclic character is not lost upon incorporation into the polymer matrix (152). The study of facilitated transport in solid state membranes indicated that fixed site complexant membranes have a long lifetime compared with liquid membranes. A recent study (150) reports the preparation of new heteropolysiloxane membrane materials, containing crown ether compounds (2,3,11,12-bis'[4-(10-aminodecylcarbonyl)}-benzo-18-crown-6 and 2,3,11,12-bis[4-(2-aminoethycarbonyl)}-

benzo-18-crown-6 compounds chemically linked in a reticulate silica matrix synthesised by the sol-gel process. The resulting heteropolysiloxanes were used to prepare dialysis membranes which presented facilitated transport of silver ions. The membranes were obtained by depositing the sol onto a planar organic support [polyvinylideneflouride (PVDF) or polysulphone (PSU)] with tape casting equipment, which permits regulation of the thickness (12μm) of the wet film. Depending on the solvent, the gel time ranged from between 1 and 2 h for tetrahydrofurane (used with PVDF) to between 6 and 12 h for ethoxyethanol (used with PSU). After deposition, the membranes were dried for 1 h at room temperature, and for 3 h at 90°C. The facilitated competitive transport of transitional metals such as Ag(I), Cu(II) is characterised by selectivity for Ag(I) ions in the range of 10-50 and transport rates (flux) for silver ions were reported in the range of 10^{-4}-10^{-3} mol/cm^{2}.24h. The authors state that these membranes differ from liquid membranes in the placement of the carrier, as fixed complexants in the solid membrane do not play the role of carrier but improve selectivity by increasing the concentration of metal ions in the membrane, which results in dual mode transport. This dual mode is based on the reversible binding equilibrium solute/complexing site and a solute diffusion between two complexing sites.

Improvement in membrane stability

A detailed review of SLM stability developments has already been published by Boomgaard et al. (30). Therefore, we shall only mention a limited number of recently published studies which cast light on the latest improvements. As suggested by several researchers, solvent characteristics that influence the stability of the membrane are surface tension and water solubility (153-155). Processes that destabilise liquid membranes are the loss of membrane material due to osmotic (156) or hydrostatic (157) pressure differences over the membrane formation of emulsions or formation of inverted micelles. An organic membrane solvent, NPOE, was recommended by Reinhoudt et al. (157) owing to its having such favourable physical properties as high lipophilicity, low viscosity and high polarity. Membrane instability due to leaching of the carrier into the aqueous phases was studied in detail by them. The authors report that this phenomenon is closely related to the lipophilicity of the carrier. Enhancement of lipophilicity was achieved by attachment of carriers to a polymeric backbone (158) or covalent linkage of aliphatic chains to the carriers (159, 160). Recently, both the stability of the membrane phase and the solubility of the carrier were improved by attachment of one or more solvent molecules to the carrier (161). The authors demonstrated the long-term membrane stability for a period of more than 5 weeks which could be achieved with a carrier concentration of up to 50 wt%. Shukla et al. (155a) proposed the mixture of diluents for improving the performance of liquid membranes while performing the permeation of U(VI) from 3 M HNO_3

with DC18C6 into the receiving phase 0.3 M HNO_3 (stripping phase). Mixtures of toluene and o-dichlorobenzene were employed to improve the stability of SLMs owing to the higher boiling point of o-dichlobenzene and its poor aqueous solubility. The permeability coefficient remained constant for more than one week without the source and receiving phase solutions being replaced. Similarly, the influence of several properties of the diluents on the stability of SLM as well on water transport was analysed by Dozol et al. (155b). The high interfacial tensions and low water solubilties were reported the principal characteristics of the membrane solvents together with their surface tension being lower than the critical surface tension of the support, which permits a long life time. Under their working conditions (osmotic pressure gradient across the membrane and the use of solid support) a membrane life time of over 200 h was achieved by using a membrane solvents with a water solubilty lower than 12 g/L and, simultaneously, a drop point of the SLM higher than 1.1 bar. These conditions could be obtained with isotridecanol or with aromatic diluents having aliphatic groups of six or more carbon atoms (like hexylbenzene) with a long chain alcohol as a phase modifier.

A recent study carried out by Szpakowska and co-workers (162) performed with Cu(II) across SLMs using Acorga 50 as carrier proposed a new method to estimate SLM lifetime based on kinetic analysis. SLM lifetime was reported as clearly depending on both the type of polymeric support and the nature of the liquid membrane. This suggests that solute-solvent (and polymer-solvent) interactions are the major factors in membrane stability. In this study, it was shown that water transport, if it occurs, does so only through empty pores of the polymeric support. No clear effect of osmotic pressure gradient on liquid membrane stability was observed.

To overcome these problems, studies were carried out on continuous regeneration and prolongation of SLM lifetime (163-164). A flat sheet SLM was used by Takahashi and Takeuchi (164) in horizontal configuration, in which a small amount of membrane solution was forced to flow with the recovery solution to stabilise the SLM. In addition, a vertical hollow fibre SLM module was used where the membrane solution was supplied by buoyant force to the pore-continua within the supporting solid. The refilling of the pores of the solid support with membrane solution was attempted by continuously supplying the solution (163). Similarly, continuous reimpregnation mode was adopted by Chiarizia and co-workers (165) when they performed uranium removal from contaminated ground water using hollow fibre modules. The LM phase reservoir was placed on top of the vertical membrane module to impregnate the hollow fibre lumens by gravitational and capillary forces.

To identify several factors responsible for SLM instability, Zha and associates (166) described the use of impedance spectroscopy coupled with the SLM technique. The advantages of this technique were reported to be that it is non-invasive and capable of providing continuous monitoring of SLM stability. The electrical impedance of an SLM over a range of frequencies was used to characterise the capacitance and conductance properties of the individual substructural layers within the SLM, provided that they have sufficiently different dielectric and/or conductance properties. If the dielectric constant (or permittivity) of the SLM is ε_m, the capacitance, C_m, is related to the area A and the thickness δ of the SLM via the relation:

$$C_m = \varepsilon_m \varepsilon_0 A/\delta$$

where ε_0 is the permittivity of the vacuum space and $\varepsilon_0 = 8.85418\ 10^{-12}$ F/m. The effective area and thickness of an SLM change as the membrane liquid is lost to the adjacent aqueous solutions, resulting in a change in capacitance. Also, the dielectric constant of the decayed membrane is usually quite different from that of the original SLM. Therefore, from measurement of the change in the capacitance and/or conductance of an SLM over time, it should be possible to characterise the process of membrane liquid loss.

Zha et al. (167) proposed an equation to estimate critical displacement pressure. The authors reported that the maximum pressure difference that an SLM can resist is related to the maximum pore size and pore structure of the membrane and the surface properties of the liquid-liquid-solid system. The value of the critical displacement pressure (P_c, kPa) can be estimated by the following equation, which is based on the new neck model:

$$P_c = \frac{2\gamma \cos(\theta_{R,i} + \alpha)}{r\left[1 + \frac{R}{r}(1 - \cos\alpha)\right]}$$

where r and R are two characteristic parameters of a membrane, $\theta_{R,i}$ the contact angle in the impregnating phase (degree), γ the interfacial tension and α the structure angle (degree). *r* measures the narrowest neck in the pores which are the widest in the membrane, and R is the radius of curvature connected with the neck, its value reflecting whether the connection is round or sharp. The maximum structure angle of a membrane is an important factor controlling critical wettability of the membrane.

Modelling of LM processes

Before scaling up any LM configurations as a hollow fibre membrane extraction or spiral wound, a theoretical model of the liquid membrane system is needed in order to design an efficient recovery process in terms of improved stability. Similarly, it is very important to elucidate the mechanisms of both the extraction of metal with extractant and the stripping of metal with stripping agent. In recent years, a number of researchers have also placed emphasis on modelling the mass transfer of metal species through HFSLMs, HFCLMs, BLMs and ELMs

Table 9

Details of recent published work on modelling of Non-despersive hollow fiber solvent extraction, ELMs, HFCLMs and BLMs

LM configuration	Metal-carrier complex	Diluent	Membrane details	Reference
Non-despersive hollow fibre SX	Cu-LIX84 Cr-TOA	n-heptane xylene	Celgard hollow fibre X-20	80a
Non-despersive hollow fibre SX	Cr-Aliquat-336	Kerosene + isodecanol	X-10 polypropylene	169
Non-despersive hollow fibre SX	Cr-Aliquat-336	Kerosene + isodecanol	X-10 polypropylene	170
ELM	La, Pr, Nd-PC88-A	n-heptane	PC88A-$2C_{18}\Delta^9$GE	171
ELM	As-EHA	n-heptane	ECA4360J	172
HFCLM	Cu-LIX-64	n-heptane	Hollow fibre,	80
	Cr, Hg-TOA	xylene	Celgard X -10	
HFCLM	Cu-LIX-84	kerosene	Celgard X-10	81
	Zn-D2EHPA	kerosene	Celgard X-10	
	Cr-TOA	heptane	Celgard X-10	
BLM	K-DC18C6	1, 2dichloroethane	DC18C6/diluent	173
	K-DB18C6	1, 2dichloroethane	DB18C6/diluent	
BLM	Y-PC88A	Xylene	PC88-A/Xylene	174
BLM	Ag-DC18C6	Dichloromethane	DC18C6/diluent	175

(80-81, 168-175). Table 9 summarises a limited number of the latest references for HFSLMs, ELMs, HFCLMs and BLMs on mass transfer modelling. Subsequently, the final equations for calculating mass transfer coefficients, permeability coefficients and flux for HFSLMs by several researchers are summarised in Table 10 (168, 176-177). Finally, values of the aqueous diffusional resistances, membrane diffusional resistances, thickness of aqueous boundary layer and diffusivity of different metal ions for different FSSLMs are summarised in Table 11 (178-189).

Table 10

Overall mass transfer coefficients, individual coefficient, permeability coefficient and flux for different conditions suggested by Sirkar[1], Danesi[2] and Izatt[3]

Non-desperisve solvent extraction	$\frac{1}{K_0} =$	$\frac{1}{K_w} =$
Membrane type and form[a]		
Hydrophobic flat	$\frac{1}{K_{io}} + \frac{1}{K_{imo}} + \frac{m_i}{K_{iw}}$	$\frac{1}{m_i k_{io}} + \frac{1}{m_j k_{imo}} + \frac{1}{k_{iw}}$
Hydrophobic HFM[a]		
Aqueous in tube	$\left(\frac{d_{ti}}{d_{to} k_{ios}} + \frac{d_{ti}}{d_{tlm} k_{imo}} + \frac{m_i d_{ti}}{d_{ti} k_{iwt}}\right)$	$\left(\frac{d_{ti}}{m_i d_{to} k_{ios}} + \frac{d_{ti}}{m_i d_{tlm} k_{imo}} + \frac{d_{ti}}{d_{ti} k_{iwt}}\right)$
Organic in tube	$\left(\frac{d_{to}}{d_{ti} k_{iot}} + \frac{d_{to}}{d_{tlm} k_{imo}} + \frac{m_i d_{to}}{d_{to} k_{iws}}\right)$	$\left(\frac{d_{to}}{m_i d_{ti} k_{ios}} + \frac{d_{to}}{m_i d_{tlm} k_{imo}} + \frac{d_{to}}{d_{to} k_{iws}}\right)$
HFSLM		
Once-through mode[b]	(a)Low metal concentration	(b)High metal concentration loaded carrier
	$C_{out} = C_{in}\left(\frac{\phi - 1}{\phi + 1}\right) \text{for} \phi \rangle 1$ $\phi = \frac{R\ddot{U}}{P^* L\varepsilon}$	$C_{out} = C_{in} - \frac{[\bar{E}]2L\varepsilon}{n\Delta_o^* UR}$ $\frac{[\ddot{E}]2L\varepsilon}{n\Delta_o^* \bar{U}R} << C_{in}$
Recycling mode[b]	(a) Low metal concentration	(b) High metal concentration loaded carrier
	$\ln\frac{C_{in}}{C_{in}^o} = -\frac{A}{V} P^* \frac{\phi}{\phi + 1} t$ $\phi > 1$	$C_{in} = C_{in}^o - \frac{[\bar{E}]A}{n\Delta_{o*} V} t$ $\frac{[\bar{E}]A}{n\Delta_{o*} V} t << C_{in}^o$
The shape factor Relationship[c]	$J_{cylindrical} = J_{planer} \frac{1}{R_o \ln\left(\frac{R_o}{R_i}\right)}$	

Source : a, Ref[1]. 176; b, Ref[2]. 168; c, Ref[3]. 177.

Table 11

Values of Δ_a, δ_a, Δ_o, D_o and d_o obtained for SLMs for different metal-carrier complexes by various researchers

Metal-carrier Complex	Δ_a s cm^{-1}	d_a cm	Δ_o s cm^{-1}	D_o cm^2s^{-1}	d_o cm	Support	Reference
Zn-Cyanex 272[a]	2.55 10^{3}	1.84 10^{-2}	1.60 10^{5}	1.56 10^{-8}	0.25 10^{-2}	C2500	178
DC18C6-Sr	2.3 10^{3}	2.3 10^{-2}	1.37 10^{3}	3.7 10^{-6}	0.25 10^{-2}	C2500	179
DtBC18C6-Sr	2.3 10^{3}		1.66 10^{3}	3.04 10^{-6}	0.25 10^{-2}	C2500	180
tBuB21C7-Cs	2.3 10^{3}		2.05 10^{3}	2.44 10^{-6}	0.25 10^{-2}	C2500	181
B21C7-Cs(ndec)	2.3 10^{3}		2.35 10^{3}	2.09 10^{-6}	0.25 10^{-2}	C2500	182
Au^{3+}-thiourea	9.1 10^{2}		9.47 10^{4}	1.32 10^{-7}	12.5 10^{-3}	Durapore	183
Am^{3+}-CMPO	4.2 10^{-6}	2.5 10^{-3}		2.4 10^{-6}[b] 1.6 10^{-6}[c]	0.48 10^{-2}	Accurel-BS7C	184
Ag^{+}-DTPA		6 10^{-3}		2.0 10^{-6}	0.25 10^{-2}	C2400	185
Zn-D2EHPA	1.2 10^{3}			2.64 10^{-6}	1.25 10^{-2}	Durapore	186
Co-mono ester[d]				6.66 10^{-6}	1.25 10^{-2}	Durapore	186
Ni-mono ester[d]				3.7 10^{-6}	1.25 10^{-2}	Durapore	186
Co(II)-D2EHPA	1.5 10^{4}		2.26 10^{5}		0.25 10^{-2}	C2500	187
Au-Phospholene	1.23 10^{2}	0.9 10^{-3}	4.95 10^{2}	1.0 10^{-6}	0.9 10^{-3}	Durapore	188
Eu^{3+}-D2EHPA	2.27 10^{2}	1.4 10^{-3}	1.15 10^{4}	2.0 10^{-7}	1.4 10^{-3}	C2500	189

a, at high concentration of carrier and high pH

b, extractant concentration <0.1 M

c, extractant conentration = 0.5 M

d, (2-ethylhexyl) phosphoric acid, mono (2-ethylhexyl) ester

In a very recent study, Szpakowska et al. (190) proposed a new method for estimating diffusion layer thickness in bulk liquid membrane and characterising unknown porosity of polypropylene supports. The following formula was proposed for calculating the unknown mean porosity factor of Celgard 4400 where the other details of Celgard 2400 were known.

$$q_{4400} = \left[\frac{J^{4400}_{App}\, l_{4400}}{J^{2400}_{As}\, l_{2400}}\, q_{2400} \right]^{1/2}$$

where l_{2400} and l_{4400} are the geometrical thickness of the membrane supports Celgard 2400 and Celgard 4400 respectively, and q_{2400} and q_{4400} stand for the porosity factor of Celgard 2400 and Celgard 4400 respectively. J^{4400}_{App} and J^{2400}_{As} are the respective copper fluxes obtained with Celgard 2400 and Celgard 4400 in SLM studies. Similarly, Cussler et al. (191) reported the effects of polydisperse hollow fibres on the performance of hollow fibre modules. They proposed a new theoretical approach to estimate the average mass transfer coefficient in a hollow fibre module from the average properties of the hollow fibres. The analysis was performed assuming that each solute diffuses independently, and that solute transport is unaffected by mass transfer resistances on the permeate side of the membrane. For polydisperse fibre diameters, the average mass transfer coefficient is reduced by the polydispersivity; for polydisperse fibre wall thickness, the average coefficient could be increased or decreased. For polydisperse hollow fibre radii, the change will be ca. 40% when the radii have a standard deviation of ca. 20%. For polydisperse hollow fibre walls, the changes are smaller. The following equation was proposed for a module with *n* different batches of hollow fibres. The radii of a given batch are all equal but the different batches have different radii. Thus the distribution is not anywhere near Gaussian, but rather a group of Dirac delta functions. In this case, the average overall mass transfer coefficient ⟨K⟩ can be calculated by

$$\frac{\langle K\rangle}{P/\delta} = \left(\frac{\sum_{i=1}^{n} \phi\sigma_i^4}{\sum_{i=1}^{n} \phi\sigma_i^2} \right) \left[1 + \frac{1}{\ln \dfrac{c_{10}}{c_{il}(\langle R\rangle)}} \times \ln \left\{ \frac{\sum_{i=1}^{n} \phi\sigma_i^4}{\sum_{i=1}^{n} \phi\sigma_i^4 \exp\left[-\ln \dfrac{c_{10}}{c_{il}(\langle R\rangle)} \left(\sigma_i^{-3} - 1\right) \right]} \right\} \right]$$

where $\sigma_i (= R_i/\langle R\rangle)$ denotes the dimensionless radius of batch i, and $c_{il}(\langle R\rangle)$ is the outlet concentration of a fibre of overall radius, σ_i the ratio of batch 'i' radius to overcome radius, c_{10} the inlet concentration, ϕ the fraction of monodisperse fibres in batch 'i', R the radius of one fibre and ⟨R⟩ the average fibre radius, and δ the wall thickness of one fibre.

The mass transfer modelling of emulsion liquid membranes was performed by Huang and associates (172) using various differential algebraic equations by selecting arsenic removal from water as a representative case. The experimental details of the emulsion composition are given in Table 9 while citing reference 172. Unlike previous ELM models, from which solutions were obtained quasi-analytically or numerically, the solution of their model was reached analytically by taking into account the following: mass transfer of the solute across the film between the external phase and the membrane phase; chemical equilibrium of the extraction reaction at the external phase-membrane interface; simultaneous diffusion of the solute-carrier complex globules of the membrane phase and stripping of the complex at the membrane-internal phase interface; and chemical equilibrium of the stripping reaction at the membrane-internal phase interface. Experimental data were obtained for arsenic concentration in the external phase versus time. The authors claimed satisfactory prediction of the experimental data when the analytical solution was applied with parameters estimated independently.

Recently, membrane processes were simulated using the gPROMS (general Process Modelling System) (192, 193) software package. This package provides a high level language for the declarative description of mathematical models of unit operations, which can then be combined hierarchically to form descriptions of entire processes. The mathematical models used may involve mixed sets of non-linear integral, partial and ordinary differential and algebraic equations. Therefore both distributed (e.g. membrane modules) and lumped (e.g. storage tanks) unit operation could be described. In simple terms, gPROMS is a process simulator able to solve mathematical equations, which need to be introduced as a model of the system. Alonso et al. (45), have been developing the modelling of LM processes using this simulator to solve the mathematical equations coming from the mass balances in hollow fibre devices. A database incluiding thermodynamical properties (equilibrium /partition coefficients) and mass transfer parameters is not available yet. gPROMS automatically constructs the mathematical model of the entire process under consideration from the models of the individual components and the appropriate connectivity relations. It then applies a combination of symbolic, structural and numerical techniques to reach its solutions. The user is shielded from much of the mathematical complexity and can therefore concentrate on the underlying modelling issues. Once a complete gPROMS model of the process is available, it is possible to carry out steady state and dynamic simulation by specifying the equipment being simulated, the values of the parameters and input variables, the initial state of the system and any external action imposed on it. For distributed unit operations, one also needs to specify the approximation method to be applied to each of the spatial domains and the granularity and order of approximation (169). Recent studies for the modelling and mass transfer of Cr(VI) with Aliquat-336 (169) and Cd(II) with Cyanex 302 (45) were performed with hollow fibre utilising gPROMS, and reasonable agreement between model predictions and experimental measurements was obtained.

In context to the experimental details furnished in earlier section on facilitated transport of ions across fixed-site carrier membranes, modelling details will be described in the following section. Some models have been developed to describe facilitated transport of ions across fixed-site carrier membranes (195-199). Most of the published papers on modelling (196-199) have proposed different mechanisms with the help of the theory pertaining to gases transport. Hence, it is out of the scope of this review. Few papers on fixed site carrier membranes, dealing with metal ions, described the permeation mechanism (149-150). The mechanism is based on an additional equilibrium inside the membrane corresponding to a global cation exchange between anion (such as picrate) and carrier sites (like neutral crown ether). After cation complexation on carrier sites, they are released into the receiving phase because of the concentration gradient between both aqueous phases. As the carrier molecules are not mobile inside the solid membrane structure, the postive charge of the cation has to be balanced by a negative charge during transport from one carrier site to another carrier site. The anions with their delocalized charge are supposed to play this role. Further, Cussler and co-workers (195) developed a model assuming that transport only takes place if two carrier moieties are close enough to allow direct solute jumping. This implies the presence of a percolation threshold. Furthermore, Noble (196-199) developed a model based on the possible diffusion of the solute between two carrier sites, and no percolation threshold is predicted.

SUMMARY

Liquid membranes have continued to command significant attention over the last few years in the field of the environment and hydrometallurgy. More promising results have been achieved when applied to separation and pre-concentration steps in analytical schemes pertaining to transduction mechanisms in chemical sensors based on transport of the active component through the membrane between sensors and sample. In supported membranes such as HFSLMs (continuous organic flow) or HFCLMs, this process still offers a solution for practical applications. These liquid membrane configurations will definitely play an important role in metal separations, particularly in situations where other conventional chemical separation techniques fail to provide a solution. ELMs with modified surfactants seem to be efficient and fast but they need to be tested on a larger scale. In spite of the satisfactory performance of ESPLIM, its practical application is limited owing to the high voltage and complicated set-up. The PIM has proved to be quite useful on a laboratory scale as this technique can certainly overcome some of the shortcomings of SLMs, such as leachability, dissolution and condensation of carrier from the membrane. This technique also needs to be tested on a larger scale. The hybrid techniques are still at the research and development stage but are quite informative for the prediction of stability aspects and future trends in LM studies.

FUTURE DIRECTION

In future, research is necessary to develop new complexation chemistry to increase the number of separation possible based on dispersion-free membrane extraction or hollow fiber contained liquid membrane techniques. Further, in addition to various membrane related parameters, study of temperature gradient as a driving force between the two sets of fibres could be a interesting. More details on rheology of emulsions formulated with the help of newly developed surfactants are needed in order to carry out scaling up studies. In PIM, future work should be performed using hollow fibre and spiral wound geometry in order to check viability of these thin membrane with respect to mechanical strength. More fundamental research is needed to understand the functioning of reverse micelle and its related phenomena. Until now, very few investigations are carried out for metal separation using RM as compare to their application for removal/separation of organic compounds. Hence, this technique should be elaborately examined particularly for metal separation in order to check their viability and effectiveness.

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TRADE NAMES AND ABBREVIATIONS

ACORGA P-500	Commercial aldoxime
Alamine 336	Mixture of trioctyl and tridecyl amine
AOT	di-2ethylhexyl sulphosuccinate sodium salt
Aliquat-336	Tridodecylammonium chloride
Bathocuproine	4,7-diphenyl-2,9-dimethyl-1,10-phenanthroline
Bathophenanthroline	4,7-diphenyl-1,10-phenanthroline

B21C7	Benzo-21-crown-7
CDTA	Trans-cyclohexanediamine tetra acetic acid
CMPO	Octyl (phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide
CTA	Cellulose triacetate
Cyanex 302	Bis-(2,4,4 trimethyl pentyl) monothiophosphinic acid
Cyanex 272	Bis-(2,4,4 trimethyl pentyl) phosphinic acid
$C_{12}EO_4$	tetraethylene glycol dodecyl ether
$2C_{18}\Delta^9SA$	Sodium dioleyl sulphosuccinate
$2C_{18}\Delta^9PA$	Dioleyl phosphoric acid
$2C_{18}\Delta^9CA$	Glutamic acid dioolyl ester succinic amide
$2C_{18}\Delta^9GEC_2QA$	Diolylglutamic acid quaternary ammonium chloride
DC18C6	Dicyclohexano-18-crown-6
DtBuC18C6	di-tert-butylcyclohexano-18-crown-6
DHDECMP	Dihexyl N,N-diethylcarmamoylmethylenephosphonate
NDecB21C7	n-decylbenzo-21-crown-7
D2EHPA	di-(2-ethylhexyl) phosphoric acid
DEPA	Bis(2-diethylhexyl) phosphate
DTMPPA	di-(2,4,4-trimethyl pentyl) phosphinic acid
DTPA	di-(2-ethyl hexyl) dithio phosphoric acid
EDTA	Ethylenediaminetetraacetic acid
EHA	2- ethylhexyl alcohol
Hinokitiol	β-isopropyltropolone
HQ	8-hydroxyquinoline
C_{11}-HQ	7-(4-ethyl-1methyloctyl)-8-hydroxyquinoline
Kryptofix 22D	1,10-didecyl diaza-18-crown-6
LIX 54	40% β- hydroxyoxime in kerosene
LIX 63	Commercial hydroxyoxime
LIX 65 N	2-hydroxy5-nonyl benzophenone oxime
LIX 84	Anti-2 hydroxy-5-nonyl-acetophenone oxime
LIX 860	β hydroxy oxime
MES	Morpholino ethane sulphonic acid
MSP-8 or MTPA	di-2ethylhexyl monothio phosphoric acid
PVC	Polyvinyl chloride
NPOE	o-nitrophenyl octyl ether
PC-88 A	2-etyl hexyl phosphonic acid mono 2-ethylhexyl ester

P 507 or P 5709	Dialkyl phosphonic acid extractant (details not provided in referred literature)
TBEP	Tris(2-n-butoxyethyl) phosphate
TBP	Tributyl phosphate
TDA	Tridecylamine
TIBPS	tri-isobutylphosphine sulphide
TOA	Tri-n-octyl amine
TOMAC	Trioctylmethylammonium chloride
TOPO	Trioctyl phosphine oxide
THAC	Tetra-n-heptylammonium chloride
Tiron	4,5-dihydroxy-1,3-benzene disulphonic acid

List of Symbols used in Equations and Tables

C_s	Concentration of surfactant (mol m^{-3})
C_{sc}	Critical concentration of surfactant (mol m^{-3})
C_{in}	Concentration of metal species at the entrance of HFSLM module (mol m^{-3})
$C^0{}_{in}$	Concentration of metal species at the entrance of HFSLM module at time zero (mol m^{-3})
d_p	Sauter diameter of internal water drop at initial time, m
d_r	Sauter diameter of internal water drop at time t, m
d_{ti} or R_i	Hollow-fibre inside diameter, L
d_{to} or R_o	Hollow-fibre outside diameter, L
E	Applied voltage, KV
$\overline{E}$	Total concentration of carrier in the liquid membrane (mol m^{-3})
K_o	Overall mass transfer coefficient based on organic phase, l/t
K_w	Overall mass transfer coefficient based on aqueous phase , l/t
K_{me}	Membrane mass transfer coefficient, m/s
k_b	Break-up rate constant of ELM, s^{-1}
k_{im}	Membrane mass transfer coefficient for species, i, l/t
k_{io}	Local mass transfer coefficient of species i n organic phase, l/t
k_{iw}	Local mass transfer coefficient of species i in aqueous phase, l/t
k_{bc}	Break-up rate constant of ELM at critical concentration of surfactant concentration, s^{-1}
K_1 and K_2	Correlation coefficient
K_{ms}	Mass transfer coefficient in stripping modules, m/s

K'_e	Equilibrium constant of extraction reaction, mol^{-2}/l^{-2}
L	Hollow fibre length, m
Δ^*_a	Aqueous diffusional parameter, s cm^{-1}
Δ^*_o	Membrane diffusional parameter, s cm^{-1}
A	Total area of perforated baffle plate or total internal area of fibres, m^2
h	Height of the perforated plate, m
J	Mass transfer flux, mol $m^{-2}s^{-1}$
k_w	Interfacial mass transfer coefficient for extraction, m/s
k'_w	Interfacial mass transfer coefficient for stripping, m/s
l	Planar diffusion path length (m)
m_i	Distribution coefficient for species, i
n	Number of metal ions bound to each carrier molecule
Q	Flow rate of feed solution, m^3/s
Q′	Flow rate of stripping solution, m^3/s
P	Permeation constant of the perforated baffle plate, m/s
P^*	$K_d/K_d\Delta_a^*+\Delta_o^*$, modified permeability coefficient, m/s
S	Cross section area of the extraction cell, m^2
S′	Cross section area of stripping cell, m^2
T	Temperature of emulsion, K
t	Time, s
t_b	Time for phase separation of emulsion, s
$\bar{U}$	Linear flow velocity of feed solution, m/s
V	Volume of the aqueous feed solution, m^3
V_{wi}^o	Initial content of water at, m^3
V_{wi}	Content of water at time, t, m^3
x	Metal concentration in the aqueous phase in the extraction cell, mol/l or kg-mol/m^3
y	Metal complex concentration in the oil phase, mol/l or kg-mol/m^3
z	Metal concentration in the aqueous phase in the stripping cell, mol/l or kg-mol/m^3
a	Specific extraction area, m^{-1}
a′	Specific stripping area, m^{-1}

Greek Letters

δ	Wall thickness of one hollow fibre
λ	Porosity of perforated baffle plate
φ	Volume fraction of water phase in emulsion
μ	Viscosity, cP
ε	Membrane porosity

Subscripts

e	Extraction
i	Interface between two phases, species i in hollow fibre section
f	Inlet
p	Outlet
s	Stripping
w	Aqueous film
m	Membrane
o	Organic, outside surface
s	Shell side
t	Tube side

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