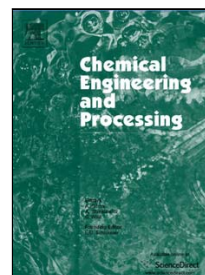


Accepted Manuscript

Title: RECENT ADVANCES IN SMART INTEGRATED
MEMBRANE ASSISTED LIQUID EXTRACTION
TECHNOLOGY

Authors: Anil Kumar Pabby, Biswajit Swain, Ana Maria Sastre



PII: S0255-2701(17)30486-5
DOI: <http://dx.doi.org/doi:10.1016/j.cep.2017.06.006>
Reference: CEP 7009

To appear in: *Chemical Engineering and Processing*

Received date: 16-5-2017
Accepted date: 20-6-2017

Please cite this article as: Anil Kumar Pabby, Biswajit Swain, Ana Maria Sastre, RECENT ADVANCES IN SMART INTEGRATED MEMBRANE ASSISTED LIQUID EXTRACTION TECHNOLOGY, Chemical Engineering and Processing <http://dx.doi.org/10.1016/j.cep.2017.06.006>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

RECENT ADVANCES IN SMART INTEGRATED MEMBRANE ASSISTED LIQUID EXTRACTION TECHNOLOGY

ANIL KUMAR PABBY^{*a}, BISWAJIT SWAIN^b AND ANA MARIA SASTRE^c

^aTRP, Nuclear Recycle Board, BARC, Tarapur, Distt. Palghar, 401502, Maharashtra, India Email: (dranilpabby@gmail.com)

^bINRPC, Nuclear Recycle Board, BARC, Tarapur, Distt. Palghar, 401502, Maharashtra, India

Email: (bswainbarc@gmail.com)

^cDepartment of Chemical Engineering, Universitat Politècnica de Catalunya

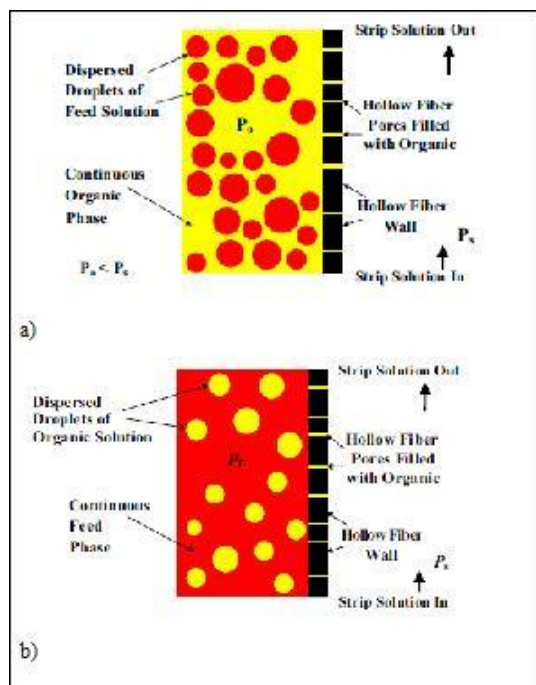
ETSEIB Diagonal 647, 08028 Barcelona, Spain

Email: ana.maria.sastre@upc.edu

*Author for communication

Graphical abstract

Novel processes based on SIMALE have been proposed as effective methods for the selective separation of different chemical species such as metal ions, organic/ biologically important compounds and gas mixtures from different waste streams including nuclear waste. This review discuss important applications including scale up, process intensification aspects, current status of the technology and future directions.



Highlights

- Smart Integrated Membrane Assisted Liquid Extraction (SIMALE) technique playing an important role as a extraction /separation of metal, organic pollutants and gases
- Remediation of nuclear waste generated in reprocessing plant by hollow fiber non-dispersive solvent extraction and hollow fiber strip dispersion
- The stability of the SLM is ensured by a modified SLM with hollow fiber renewal liquid membrane and polymer inclusion membrane
- Ionic liquid based membrane extraction and super critical fluid based membrane are promising future separation techniques.

Abstract

Novel processes based on SIMALE have been proposed as effective methods for the selective separation of different chemical species such as metal ions, organic/ biologically important compounds and gas mixtures from different waste streams including nuclear waste. The industrial use of supported liquid membranes based on conventional liquids is limited by their relative instability and short lifetime. Under SIMALE techniques, the stability of the SLM is ensured by a modified SLM with pseudo emulsion based hollow fiber strip dispersion or non-dispersive solvent extraction techniques. In order to promote operational stability, SIMALE, using ionic liquids, as a liquid membrane phase could overcome these inconveniences due to their negligible vapour pressure and the possibility of minimizing their solubility in the surrounding phases. SIMALE studies on membrane-based dense gas extraction reported higher extraction efficiencies when the near critical or supercritical solvent is used. This review also discuss important applications including scale up, process intensification aspects, current status of the technology and future directions.

Abbreviations:

E	:	Extracting solvent
S	:	Stripping Chemical
K	:	Overall mass transfer coefficient (m/s)
K_f	:	Feed mass transfer coefficient (m/s)
K_e	:	Extraction reaction kinetic coefficient (m/s)
K_{be}	:	Back Extraction (Stripping) kinetic coefficient (m/s)
K_m	:	Membrane mass transfer coefficient (m/s)
K_s	:	Strip mass transfer coefficient (m/s)
K_m^*	:	Gas filled pore membrane mass transfer coefficient (m/s)
K_m^o	:	Stagnant membrane layer mass transfer coefficient (m/s)
d_{in}	:	Non wetted logarithmic mean diameter, (m)
d'_{in}	:	Wetted logarithmic mean diameter, (m)
e	:	Enhancement Factor
H	:	Henry's Constant
d_i	:	Inner diameter of hollow fiber lumen (m)
d_o	:	Outer diameter of hollow fiber lumen (m)
d'_{in}	:	Logarithmic mean diameter of none wetted of the membrane (m)
H	:	Henry's constant
TOPO	:	Tri-n-octylphosphine oxide
DNPPA	:	di-nonyl phenyl phosphoric acid

7. NOMENCLATURE, LIST OF SYMBOLS, AND ABBREVIATIONS

Nomenclature:

Alamine 336	tertiary amine,[tri-(C8–C10) amine]
Aliquat-336	Tricaprylylmethylammonium chloride
Cyanex 272	Bis(2,4,4-trimethylpentyl) phosphinic acid
DHOA	<i>N,N</i> -di- <i>n</i> -hexyl octanamide
D2EHPA	Di(2-ethylhexyl) phosphoric acid
LIX 984N	1:1 (v/v) mixture of LIX 84-I and LIX 860N-I
MIBK	Methyl isobutylketone
nph	Normal paraffin hydrocarbon
PEI	Polyethylenimine
PEN-G	Penicillin G
PHWR-HLW	pressurised heavy water reactor high-level waste
PHWR-SHLW	Pressurised heavy water reactor simulated high-level waste
N-235	Mixture of tertiary amine based extractant
TODGA	<i>N,N,N',N'</i> -Tetraoctyl-3-oxapentanediamide
TBP	Tri- <i>n</i> -butyl phosphate

List of symbols:

A	Geometrical surface area (cm ²)
A	Absorbance (O.D.)
C _{f,t}	Concentration of metal ion in aq. phase at time t (mol/L)
C _{f,o}	Concentration of metal ion in aq. phase at time t (mol/L)
c	Concentration of ozone (mol/L)
d	Effective diameter of membrane pore (μm)

d_{in}	HF inner diameter (cm)
d_{out}	HF outer diameter (cm)
d_{avg}	Average diameter of HF membrane (cm)
D	Diffusion coefficient in the pores (cm ² /s)
e	Extinction coefficient (-)
H	Henry coefficient (liquid-gas equilibrium constant)
K_{Total}	Overall mass transfer coefficient (m/s)
K_{SHELL}	mass transfer coefficient in shell side (m/s)
K_M	Membrane mass transfer coefficient (m/s)
K_{TUBE}	mass transfer coefficient in tube side (m/s)
l	Cell length (cm)
m_D	Equilibrium distribution coefficient between tube side liquid and shell side liquid
P	Over all permeability coefficient (m/s)
ΔP_c	Critical break through pressure (Pa)
Q	Effective surface area (cm ²)
r_p	Pore radius (cm)
V	Volume of aqueous feed (m ²)
θ	Contact angle (in degrees)
λ	Surface tension of water
ε_M	Membrane porosity (-)
τ_N	Tortuosity factor (-)

Index

Summary of Review

1. Introduction
2. Classification, methodologies and associated mechanism in smart integrated membrane assisted liquid extraction technology (SIMALE)
 - 2.1 Non-dispersive solvent extraction (NDSX)
 - 2.2 Pseudo emulsion based hollow fiber strip dispersion
 - 2.3 Hollow fiber renewal liquid membrane (HFRLM)
 - 2.4 Polymer inclusion membrane
 - 2.5 Supercritical fluids based membrane extraction
 - 2.6 Ionic liquid based membrane extraction technique
3. Application of smart integrated membrane assisted liquid extraction techniques, process intensification and stability aspects
 - 3.1 Non-dispersive solvent extraction (NDSX)
 - 3.2 Pseudo emulsion based hollow fiber strip dispersion
 - 3.3 Hollow fiber renewal liquid membrane (HFRLM)
 - 3.4 Supercritical fluids based membrane extraction
 - 3.5 Ionic liquid based membrane extraction technique
 - 3.6 Polymer inclusion membrane
4. Mathematical modeling aspects of SIMALE techniques
5. Concluding remarks and future directions
6. Acknowledgements
7. Nomenclature and list of symbols
8. References

1. INTRODUCTION

Membrane separation is an energy efficient-technology, which is widely used for a large number of industrial applications, such as sea water desalination, natural gas conditioning, and waste water treatment etc. including removal of radionuclides from radioactive waste streams with the view to give clean environment [1]. It is important to note that the efficiency of separation processes strongly depends on the proper selection of membrane material and membrane configuration. Of course, some improvements in separation performance can also be achieved by optimization of the

module design or recycling of different streams by cascade system. At the same time, for different applications the membrane should face inherently different requirements. Although the increasing demand for raw materials, energy and products under the constraints imposed by sustainable development is a complex problem, a possible solution is found by the intensification and integration of industrial processes which offer solutions to increase competitiveness and efficiency without neglecting the protection of the environment [2, 3]. Drioli et al. [4] define process intensification as the strategy to bring drastic improvements in manufacturing and processing by decreasing capital cost, equipment size, energy consumption, waste production, environmental impact, etc. In this context, membrane operations have the potential to replace conventional energy-intensive techniques, accomplish the selective and efficient transport of specific components, improve the performance of reactive processes and, ultimately, provide reliable options for a sustainable growth [5]. In addition membrane processes can be beneficially integrated at different levels because of their several advantages over conventional processes: compactness, easy scale-up and automation [6]. In particular, liquid membrane technology incorporating selective carriers is strongly related to the process intensification strategy due to the benefits derived from the facilitated transport of a solute resulting from the coupling between chemical reaction and mass transport phenomena [7]. **Fig. 1** shows mass transport through liquid membranes and compares a pure diffusion-type process (**Fig. 1a**) with a simple facilitated transport mechanism (**Fig. 1b**) where the solute has first to react with the carrier to form a solute-carrier complex, which then diffuses through the membrane to finally release the solute at the permeate side [8]. As it is depicted in **Fig. 1**, the use of appropriate reacting agents in the liquid membrane formulation allows the intensification of the extraction and stripping stages since the driving forces across the membrane in smart integrated membrane assisted liquid extraction (SIMALE) type of techniques are higher than the concentration gradients achieved in non-reacting processes

Under process intensification strategy, the techniques used should meet the above mentioned criteria. Therefore, improved version of membrane extraction techniques named as smart integrated membrane assisted liquid extraction (SIMALE) techniques are of great interest in the field of metal separations. Among SIMALE techniques, non-dispersive solvent extraction, pseudo emulsion based hollow fiber strip dispersion, near critical or supercritical extraction using HF contactor and ionic liquid based membrane extraction have more potential in different areas with respect to chemical technologies. In SIMALE techniques, the combination of liquid membranes and membrane contactors is a suitable strategy to increase the process competitiveness in terms of process intensification due to the following reasons: (i) membrane contactors provide higher interfacial mass transfer area/equipment size ratio than conventional equipments (i.e. 30 times higher than packed towers and 10 times higher than stirred tanks for solvent extraction), (ii) the effective contact area is known, constant and independent of flow rates of the fluid phases, (iii) the non-dispersive contact between the fluid phases which flow independently is achieved avoiding additional separation stages, (iv) the modular design simplifies the process scale-up and allows to operate over a wide range of capacities and (v) in general the operation costs for membrane technologies are lower than those associated to conventional processes [1, 3].

Under first category of SIMALE, hollow fiber non-dispersive solvent extraction with one module and extraction and stripping with two separate modules is selected. Several applications have been recorded with NDSX technology, which can be divided into two groups: (a) separation of organic compounds and, (b) separation of inorganic compounds. In the first group motivating examples are: (i) separation of l-phenylalanine [9], (ii) removal of phenol, 2-chloro phenol, toluene, nitro-benzene and acrylonitrile [10], and (iii) recovery of aroma compounds from the food industry [11]. In the second group the main applications are directed at metal separation applications: (i) Separation of Co(II) and Li(I) from aqueous solution [12], (ii) simultaneous removal of arsenic and selenium from wastewater [13], (iii) separation of Ni/Cd mixtures [14], (iv) separation of uranium/ thorium from analytical waste [15] and (v) selective separation of Zn(II) over iron from spent pickling effluents [16] and pertraction of transition metal ions [17]. In a very recently published study, authors have compared extraction of cerium by hollow fiber supported liquid membrane using tri-octyl methyl ammonium chloride (TOMAC) with solvent extraction data using mixer settler. The efficiency of hollow fiber supported liquid membrane was greater than that of solvent extraction for the extraction of cerium for studied system [18].

The second category in SIMALE technique is pseudo emulsion based hollow fiber strip dispersion (PEHFSD) or emulsion pertraction technology (EPT) has been selected. Progress in knowledge about membrane-based solvent extraction has led the development of an attractive alternative in this group of technologies that is known as PEHFSD. In this configuration an emulsion phase comprising of an extractant agent and a back-extraction agent, flows through the shell side of one single HF module while the aqueous feed phase, which contains the target species, flows through the inner side of the micro porous fibers of the module (Fig. 2). The first works dealing with EPT were concerned with the extraction of Cu, Ni and Hg [19], separation of Cd/ Pb mixtures [20] and separation of hydrocarbons from wastewaters [21]. The removal and recovery of Cr(VI) from waste waters [22] and the selective separation of Zn(II)/Fe(III) mixtures in a pilot plant were also studied [23]. More recent works deal with removal and recovery of CN^- and Cd(II) and rare earths [24,25], and the recovery of Au(I) in presence of CN^- [26].

In thirds category under SIMALE, a new liquid membrane technique called hollow fibre renewal liquid membrane (HFRLM) has been reported [1, 27]. This is based on the surface renewal theory and integrates the advantages of fibre membrane extraction and liquid film permeation. In the HFRLM process, hydrophobic hollow fibres are used which are pre wetted with the organic phase so that the pores become completely filled with the organic phase. The HFRLM process schematic and mechanism are depicted in Fig. 3. The feed phase is pumped through the shell side of the module (see Fig. 3a). The stirred mixture of the organic and stripping phase, containing uniformly dispersed organic droplets, is pumped through the lumen side of the fibres. Due to the wetting affinity between the organic phase and the walls of hydrophobic fibres, a thin organic film, i.e. a liquid membrane layer, is developed within the lumen side of the fibres. The shear force resulting in the flowing fluids causes the film liquid to form micro droplets on the surface of the liquid membrane layer, which will peel off from the surface of the liquid membrane layer and enter the lumen side flowing fluid. At the same time, the organic droplets, dispersed fluid flowing in the lumen side, will fill the surface of the liquid film; thus renewal of the liquid membrane proceeds [Fig. 3b]. This effect and the huge mass transfer area due to the direct contact of organic droplets and the vigorously mixed aqueous phase can accelerate the mass transfer rate and

greatly reduce the mass transfer resistance within the lumen side. In addition, the HFRLM technique has some potential advantages of long-term stability, high mass transfer rate, easy operation, etc. The utilization of this technique is well established for metal separation and described in Refs [27-30].

Separation based on the use of polymer inclusion membranes (PIMs) is a relatively new technology under important SIMALE category for the safe and effective separation of metallic and non-metallic ionic species and small organic molecules from aqueous solutions [1, 31]. PIMs encapsulate an extraction reagent in a base polymer matrix (typically poly vinyl chloride, PVC) or ester-substituted cellulose derivatives, such as cellulose triacetate (CTA)), often in combination with plasticizers and/or chemical modifiers. PIMs have been developed as a safer alternative to liquid-liquid extraction techniques (commonly referred to as solvent extraction, SX), which often require large inventories of toxic, volatile and flammable chemicals. Many researchers have successfully adapted existing SX technologies to PIM systems [1, 32-33], and work continues towards better understanding the fundamental processes that underpin PIM extraction and transport. PIM systems rely on the use of carrier-facilitated transport, where the membrane is made permeable to the target solute only by the action of an extraction reagent; the target solute is generally reactively coupled to the extractant at the membrane-solution interface and transported into and through the membrane by diffusion of the extractant-solute complex or ion-pair. The extraction of the solute into the membrane is commonly observed by its depletion in the aqueous phase. The extraction process is a combination of physical diffusion processes inside the membrane and chemical reaction kinetics at the membrane-solution interface, which have been discussed in earlier studies [1, 34]. Development of a PIM for the preconcentration of antibiotics in environmental water samples has established its role in the field of analytical applications. [35]. In recent published study, , membrane transport of cadmium ion was explored through a polymer inclusion membrane (PIM) in micro-system. The system was composed of a flat sheet membrane sandwiched between donor and acceptor aqueous phases that flow in serpentine micro channels built in Teflon plates. Compared with conventional PIM cell, results showed by authors established the feasibility of PIM in micro device to achieve efficient Cd ions extraction [36].

In the fourth category under SIMALE, ionic liquid based membrane extraction has drawn maximum attention and achieved selective transport of metal ions, organic compounds such as amines, alcohols, organic acids, ketones, ethers, and aromatic hydrocarbons [37-40], mixed gases [41-42] and metal ions [43-44]. Ionic liquids results in the stabilization of the SLMs due to their negligible vapor pressure, the possibility of minimizing their solubility in the surrounding phases by adequate selection of the cation and anion [45], and their high viscosity (up to 500 cP) which could slow down the displacement of the liquids from the micron pores under pressure. Other interesting properties of ILs in the context of liquid membranes are their high ion conductivity [46] and high solvent power [47]. All these mentioned properties have led ILs to being considered “green designer solvents” [39]. In recent work, X-ray computed tomography scanning is utilized to analyze the three dimensional structure of hollow fiber supported ionic liquid membranes (SILMs) applied for gases separation [48]. .The experimental set-up used are similar as discussed in NDSX and EPT.

In the last category of SIMALE, one of the applications of membrane contactors is based on supercritical extraction. This process is called porocritical extraction. Porocritical process or porocritical extraction is a commercial supercritical fluid extraction (SFE) which utilizes a HFMC to contact two phases for the purpose of separation [1,2,49]. In this process a macro porous membrane provides contact between feed and solvent. The aqueous feed solution is passed on one side, while the extraction solvent, which is a near-critical or a super-critical fluid, is flowed on the other side. The aqueous solution is also maintained at a high pressure near the dense solvent to establish interface between solvent and feed. When the membrane material is hydrophobic, i.e. the aqueous solution does not penetrate the membrane pores and the gas phase can fill the membrane pores. In this process, the driving force is concentration difference of the solute between feed and dense solvent. In porocritical extraction, there are four steps for the transfer of a solute across the membrane: transport through the boundary layer of the liquid feed solution; soluble in the near critical or supercritical fluid (SCF) extraction phase; diffusion through the stagnant extraction phase within the pores; transport through the boundary layer of the extraction phase. Fig. 4 schematically shows the principles of this process. The application of SCF is described in Refs [50-54].

In recently developed new SIMALE technique,, a SLM with sorbent interface was developed and employed for Eu extraction from nitrate medium [55]. The idea was based on the SLM system with the sorbent interface. This membrane extraction system was a three-phase SLM consisting of an aqueous phase (feed phase), organic extractant/ nano sorbent (membrane phase) and aqueous phase (stripping phase). For this purpose, the multi-walled carbon nanotubes (MWCNTs) dispersed in the organic extractant (kerosene + Cyanex272) was held in the pores of a porous membrane by capillary forces and ultrasonic agitation. All experiments were performed using PTFE filter membranes. The results showed that loading of MWCNTs in the liquid membrane enhanced the permeation of Eu. The stability of the SLM was satisfactory at 10 cycles of operation.

This review focuses the recent advances of SIMALE techniques, their potential in area of metal separation (including radionuclides), gas separation and other selected applications with respect to pharmaceutical and biotech applications. This review also includes issues related to stability, long term performance and process intensification aspects using SIMALE techniques.

2.1. CLASSIFICATION, METHOLOGIES AND ASSOCIATED MECHANISM IN SMART INTEGRATED MEMBRANE ASSISTED LIQUID EXTRACTION TECHNIQUES

2.1. Non-dispersive solvent extraction (NDSX)

Non-dispersive solvent extraction technique use membrane contactors that incorporate hydrophobic hollow fibers (HF) which allow the circulation of two fluid phases, with the organic phase embedded in the pores of the HF module. Because of the hydrophobicity of the pores, mixing of the phases is not possible, allowing there to contact at the aqueous–organic interface only [1, 12]. A schematic view of the membrane-based extraction process using one and two

hollow fiber contactor in recirculation mode is shown in **Fig. 5a and 5b** respectively. Using one HF contactor, both aqueous and organic phases are contacted in a hollow fiber module in a cocurrent or countercurrent for extraction or stripping run under recirculating mode. In the extraction module, the feed aqueous phase flows through the lumen of the fibers, while the organic phase circulates through the shell side, wetting the wall of the hydrophobic fibers. The pressure of the aqueous phase was held at 0.2-0.5 bar higher than the pressure in the organic phase. Other, possible configuration is non-dispersive solvent extraction (NDSX), containing two HF modules, one module for the extraction step and one module for the back-extraction step. The aqueous phases circulate through the inner side of the fibers and the organic phase circulates through the shell side in both modules (**Fig. 5a**).

2.2. Pseudo emulsion based hollow fiber strip dispersion (PEHFSD)

The hollow fiber strip dispersion process comprises a single module for extraction and stripping. A pseudo-emulsion phase is prepared in a stirred tank, this pseudo-emulsion is formed by the organic solution and the dispersed stripping solution. Once pumped to the module for the shell side, the organic phase wets the porous wall of the fiber because of its hydrophobic nature. The feed solution is fed into the module through the tube side of the fibers. The differential pressure is always kept below the breakthrough pressure, thus in the feed phase the pressure is maintained in the range of 0.2 -0.5 bar range higher than in the pseudo-emulsion phase. The characteristics of the pseudo-emulsion should be such that it should have clear and fast (in the order of a few minutes) phase separation when mixing in the tank is stopped (**Fig. 2**). Then the recovery of the metal from the stripping solution can be achieved

2.3. Hollow fiber renewal liquid membrane (HFRLM)

In this technology, the stirred mixture of organic phase and feed phase (or stripping phase) is pumped through the tube side of the fibers, the organic phase is uniformly dispersed in the corresponding aqueous solution and wets and fills the pores of the module (**Fig. 3**). The stripping phase (or the feed phase) flows through the shell side, co- or counter currently. The flows are controlled to maintain a positive pressure on the shell side, in order to prevent penetration of the organic phase into the shell side [for more details refer section 1.0 'introduction'].

2.4 Polymer inclusion membrane (PIM)

For more clarity and information, one specific preparation is discussed in detail as representative case. Solution of cellulose triacetate as the support, the plasticizer (for example *o*-nitrophenyl pentyl ether *o*-NPPE), and any suitable extractant (for example calix [4] crown-6 derivative) [56] as the ion carrier in desired diluent (such as dichloromethane) are normally prepared for PIM applications. In next step, a specified portion of this organic solution was poured into a membrane mold comprised of a 9.0 cm glass ring attached to a glass plate with cellulose triacetate–dichloromethane glue. The dichloromethane was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion into cold water. Next, the membrane was soaked in distilled water for 12 h. Two samples of membrane were cut from the same membrane film for transport experiments. The average PIM membrane thickness

was estimated as 35 μm . After preparation of membrane, transport experiments were performed as an example to understand the phenomenon and to evaluate performance of the membrane. Transport experiments were conducted in a permeation cell in which the membrane film (at surface area of 4.9 cm^2) was tightly clamped between two cell compartments. Both, i.e. the source and receiving aqueous phases (50 cm^3 each) were mechanically stirred at 600 rpm. The receiving phase was 0.01–1.0M HCl. The PIM transport experiments were carried out at the temperature of 20 ± 0.2 $^\circ\text{C}$. Small samples of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine metal concentrations by atomic absorption spectroscopy method. The source phase pH was kept constant and controlled by pH meter.

2.5 Supercritical fluids based membrane extraction

In this process a macro porous membrane allows the contact between two phases. On one side, an aqueous liquid solution is circulated and on the opposite side the extraction solvent is a near-critical or supercritical fluid (**Fig. 4**). When the membrane used is hydrophobic, the aqueous solution does not penetrate within the membrane porosity. A meniscus is formed in the pore mouth establishing a dense gas–liquid interface. The driving force of the mass transfer process through the membrane is a concentration gradient between both circulating phases. In this operation, permeability and selectivity are defined by the transport phenomena at the proximities and through the membrane coupled to the phase equilibrium between the aqueous feed solution and the CO_2 phase. The size and number of fibers in a membrane contactor will be determined by the volume of the liquid to be treated. Previous studies on membrane-based dense gas extraction report higher extraction efficiencies when the near critical or supercritical solvent is circulated outside the fibers and the liquid feed solution is circulated in the lumen side [57-60].

2.5 Ionic liquid based membrane extraction (ILME)

Ionic liquids are formed by a nano symmetrical or unsymmetrical organic cation such as imidazolium, N-alkylpyridinium, alkylphosphonium, etc. [**Fig.6**], and different inorganic or organic anions such as halides, nitrate, tetrafluoroborate ($[\text{BF}_4^-]$), trifluoro-methylsulfonate ($[\text{OTf}^-]$), bis (trifluoromethane -sulfonyl) imide ($[\text{NTf}_2^-]$), etc. The task-specific ionic liquids (TSILs) have also been developed with specific functional groups linked by covalent bond to the anionic or, more often, cationic part of the salt [**Fig. 7**]. Very often, ILs and TSILs are used mixed with other conventional extractants in order to increase the efficiency of the extraction process. Furthermore, this new branch of reagents can extract anions and cations without using ion exchange but with ion pair mechanism. The ionic liquid membrane based extraction can be carried out in similar set-ups as described in NDSX or in HFSLM mode.

3.0 APPLICATION OF SMART INTEGRATED MEMBRANE ASSISTED LIQUID EXTRACTION TECHNIQUES (SIMALE) IN METAL SEPARATION (INCLUDING RADIONUCLIDES), GAS SEPARATION AND BIOTECHNOLOGICAL APPLICATIONS

3.1. Non-dispersive solvent extraction (NDSX)

The broad spectrum of metal extraction which have been studied with **non**-dispersive solvent extraction (NDSX) mode includes noble metals, alkaline and alkaline earth metals, rare earth, radioactive metals, heavy and toxic metals. The extraction of copper from ammoniacal aqueous solutions with LIX 54 was studied by Gameiro et al. [61] using NDSX with hollow fibres as contactors. Some equilibrium experiments for the system $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4/\text{NH}_3/\text{LIX 54}$ were carried out. Extraction studies using a single hollow fibre module showed that the rate of extraction was not significantly affected by the hydrodynamics of the phases in the range of 150–710 mL min^{-1} . The experimental overall mass transfer coefficients were compared with the ones obtained by using the conventional resistance in series model. These values were in agreement, when the concentration of LIX 54 was as high as 0.2 k mol m^{-3} and the initial concentration of copper in the feed phase was 0.3 kg m^{-3} . Thus, under these experimental conditions the extraction of process is controlled by diffusion in the aqueous boundary layer. If the concentration of LIX 54 remains in the range of 0.015–0.10 k mol m^{-3} , the extraction process will be then controlled by chemical reaction and diffusion in the aqueous boundary layer. Similar experience on HF contactors was obtained by other researchers also but SEM of the polypropylene fibers will help to understand whether morphology of the fiber is intact after long duration of use of these HF contactors.

In more detailed study, Pabby et al. performed hollow fiber non-dispersive solvent extraction with a single module (batch process) (Fig. 5a) and with two modules (Fig. 5b) (extraction and stripping together) in counter-current mode using 18% LIX79/*n*-heptane [62]. The performance of the single module has certain drawbacks such as equilibrium limitation and saturation of the extractant during the experimental run. For this reason, the extraction module failed to perform correctly in the presence of a high concentration of NaCN, and this necessitated a high concentration of LIX79 in the extraction module. However, in the integrated membrane process with two modules, saturation of the carrier does not occur as it is continuously regenerated in the stripping module, resulting in a better performance. The use of stripping solution containing NaOH provided efficient and fast back extraction of Ag (I) in the stripping module. The $K_{E,Ag}$ (mass transfer coefficient for extraction) in the extraction module was found to be greater in the integrated membrane process than in the single module operation. The rate-controlling step changed to reaction control when linear feed flow velocity exceeded 2.46 cm/s ($Re = 5.50$). On the other hand, stripping reaction was fast and instantaneous and the model presented clearly indicated that the rate controlling step in the stripping module was in the membrane and the organic solution.

Phenol and its derivatives are often present in the wastewater discharged of manufacturing processes such as in the petrochemical and agrochemical industries and in coal gasification wastewaters. Due to their potential harm to human health, most are listed as priority pollutants by the US Environmental Protection Agency. Therefore, treatment processes must often be implemented before the waste streams can be safely discharged. The next paper meets the same objective. In this study, the extraction and stripping of phenol was carried out by Shen et al. [63] in two separate hollow fiber membrane modules in co-current mode using 10% (v/v) TBP/ShellSol2046. Extraction and stripping equilibrium distributions were determined. The overall mass transfer coefficients were determined experimentally and

then compared with the predictions from the resistance in series model. The shell side mass transfer coefficients were evaluated with a modified correlation. Results showed that the overall mass transfer coefficients during extraction were about one order of magnitude greater than those obtained during stripping. The hydrodynamics of the aqueous phase on the tube side had a significant effect on the overall mass transfer coefficients in the extraction module. However, stripping profiles did not change significantly under the hydrodynamic conditions studied. The resistance of the membrane can also be minimized if hydrophilic membranes are used instead of hydrophobic membranes in the stripping module.

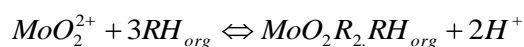
In continuation Guo et al. [64] have studied the mass transfer problems in the hollow-fiber membrane extractor module theoretically and experimentally with concurrent- and countercurrent-flow. The theoretical predictions were represented graphically with the mass-transfer Graetz number (G_z), flow pattern and packing density (ϕ) as parameters and the theoretical results were also compared with those obtained by experimental runs. The theoretical and the experimental runs showed that increasing the aqueous phase flow-rate, Cu^{2+} , $(\text{HR})_2$ concentration, and packing density can enhance the Cu^{2+} extraction rate in the liquid-liquid membrane contactor. The highest extraction rate, extraction efficiency and mass transfer efficiency can be achieved by arranging the packing density $\phi = 0.3$. The advantages and values of the present two-dimensional theoretical model claimed by author are that the extraction rate can be calculated directly without experimental runs, and the dimensionless concentration profile can be obtained in the entire membrane extractor. This type of studies will help in scale up where accurately estimation of mass transfer coefficients is required in order to calculate process efficiency and long term performance.

The role of diluents in LM is of paramount importance as long term stability will be decided by its specific chemical and physical properties. Next paper will deal with similar approach by developing LMs with vegetable oils. These are organic solvents, which can be used in SLM, as the novel and green LM. There are some advantages in comparison with other solvents such as low cost, non-hazardous, non-toxic, easily available, naturally occurring low-cost and renewable sources. A supported liquid membrane (SLM) using tri-*n*-butyl phosphate (TBP) and sesame oil as liquid membrane (LM) was examined [65]. Phenol was effectively extracted by SLM and various factors affecting phenol extraction such as initial phenol concentration, carrier concentration, feed phase pH and stripping phase concentration were investigated in details. Optimal experimental conditions for transport of phenol were obtained using analysis of variance (ANOVA) after 7 h extraction as phenol concentration of 200 mg/L; carrier concentration (%TBP) of 40%; feed phase (pH =2) and stripping phase concentration of 1.1 M NaOH. The results showed that replacement of traditional solvents such as kerosene with sesame oil can lead to higher mass transfer rate and better approach for recovery of phenol from wastewater. This study revealed that the stability of membrane increased with decreasing stripping phase concentration and carrier concentration. As observed, the higher initial carrier concentration leads to the faster SLM instability. This is because solubility of TBP in an aqueous solution is more than that of sesame oil, and thus increasing initial carrier concentration increases solubility of the LM in the aqueous solutions. Triglycerides are the main constituents of vegetable oils so increasing NaOH concentration accelerates cleavage of the ester bond and releases the fatty acid salt and glycerol. The minor change in pH before the SLM becomes instable is basically due to reduction of phenol molecules

in the feed phase as time goes on. To investigate the influence of electrolyte strength in the aqueous solutions on the membrane loss, NaCl was added to the feed solution. As observed by authors it was clear that the salt addition to the feed phase increases the SLM stability. This is due to the fact that by the salt addition to the feed phase, ionic strength of solution was increased with increasing the salt concentration. Therefore, the ionic strength difference between the stripping solution and the feed solution decreased, and this reduced the osmotic pressure between the two sides of the SLM. According to the osmotic pressure mechanism [1, 31, 56], the SLMs become more stable as the osmotic pressure difference between the two sides of the membrane decreased.

In the last two decades, considerable work has been carried out for the partitioning of minor actinides from HLLW employing many solvents in several modes such as solvent extraction, extraction chromatography (EC) and supported liquid membrane (SLM) [1,2]. Partitioning of these actinides will avoid the radiological risk due to these minor actinides during the storage of nuclear waste. If these actinides are not separated, it may leach into the environment during their long term storage also cost of their surveillance gets reduced. With regard to remediation of high level waste (HLW), the studies on the partitioning of actinides from high-level liquid waste of PUREX origin employing supported liquid membrane technique was examined by Dudwadkar et al. [66]. The process uses solution of tri-n-octyl phosphine oxide in n-dodecane as a carrier with polytetrafluoroethylene (PTFE) support and a mixture of citric acid, formic acid and hydrazine hydrate as a receiving phase. Fast separation of neptunium, uranium, plutonium and americium was accomplished using a solution of TOPO in n-dodecane at a concentration of 0.9M as carrier, while using a mixture of 0.1M citric acid, 0.4M formic acid and 0.4M hydrazine hydrate as receiving phase. Since the transport rates are found to be very low in the presence of high concentration of uranium, the present method afforded best results only after depleting the uranium content of the waste solution. This is a laboratory scale study and authors need to conduct pilot runs for evaluating its long term performance for actinide partitioning. Morphology of PTFE membrane should be checked by SEM before and after using in experiments in order to confirm any surface alteration due to exposure with alpha/gamma emitting actinides.

In this study by Rout et al., hollow fiber membrane technique was shown to have great potential for Mo recovery. In continuation of the work on NDSX, a comparative study between solvent extraction and hollow fiber membrane technique was performed for the extraction of Mo(VI) from an aqueous sulfate solution [67]. Effect of different parameters such as pH of feed solution, flow rate, extractant concentration, metal ion concentration and strip solution concentration on molybdenum extraction has been investigated. The maximum extraction of Mo(VI) with LIX 84I took place at equilibrium pH 1.3 and within this acidic pH the predominant Mo(VI) species is MoO_2^{2+} at interface, the reaction mechanism of hexavalent Mo with LIX 84I was suggested by authors as:



The molybdenum flux, J_{Mo} (mol/cm²) was increased with increase in pH and flow rate up to 1.5 and 420 mL/min., respectively and beyond that it was decreased. The separation of Mo was carried out from a solution bearing Mo, Cu, Fe, Mn, Zn, Co and Ni and the separation factor values were found in the order of $D_{Mo}/D_{Cu} < D_{Mo}/D_{Fe} < D_{Mo}/D_{Zn} < D_{Mo}/D_{Co} < D_{Mo}/D_{Mn} < D_{Mo}/D_{Ni}$. The transport of different metal ions as a function of time is shown in **Fig. 8**. To know the efficacy of molybdenum extraction using hollow fiber, two solutions of 4 L bearing 10.75 mol/m³ Mo were separately treated with conventional mixer-settler and hollow fiber module. A comparison table for both the techniques is presented in **Table 1**. So it was claimed by authors that a clean separation of molybdenum was possible from the solution bearing multi metals such as copper, nickel, cobalt, zinc, iron and manganese by the hollow fiber membrane using LIX84I.

In a very interesting application, a hollow fiber supported liquid membrane bioreactor (HFSLMB) was developed by Praveen et al. [68] for two phase biodegradation of phenol. The semi-dispersive approach stabilized the liquid membrane and facilitated non-dispersive transport of substrate from the solvent to the cells *Pseudomonas putida* could biodegrade phenol at 1000–4000 mg L⁻¹ without experiencing severe substrate inhibition. For example, 4000 mg L⁻¹ phenol was biodegraded within 76 h while the specific growth rate and biomass yield were 0.31 h⁻¹ and 0.26 g/g, respectively. Substrate removal occurred in two sequential steps: removal during log growth phase and removal under diffusion limitation. The biodegradation rates could be enhanced by changing the phase ratio, hydrodynamic conditions and the interfacial area. Repeated batch runs were conducted for more than 400 h to evaluate long term stability of the HFSLMB. Phenol bio- degradation performance of the HFSLMB was also comparable to that of other two phase partitioning bioreactors (TPPBs) operated with solid or liquid non-aqueous phases as shown in **Table 2**. Bioreactor performance deteriorated after 5 runs (approximately 100 h) due to the presence of biofilms on the membrane but a proposed 5 h washing cycle after every 100 h of operation could restore the performance. These results suggested that the HFSLMB can be a promising alternative to conventional two-phase partitioning bioreactors. The reproduction of the results in longer run will certainly establish this technique as an alternative to other conventional techniques.

In another study, HFSLM was used to extract Nd (III) at a very low concentration from nitric solution [69]. This study is primarily focused on mathematical modeling of HFSLM. Since reliable mathematical models provide an understanding of the transport mechanism of target species across liquid membrane (from the feed side to stripping side), hence they are required. The models also help in the scale-up of the HFSLM system. Most models have been developed based on the principle of a facilitated diffusional transport mechanism neglecting the chemical reactions in the system. Percentages of extraction and stripping reached 95% and 87%, respectively. Optimum conditions were achieved using 4.5 pH of feed solution, 0.5 M HEHEPA (full form and add in list), 4 M HNO₃, and equal flow rates of both feed and stripping solutions at 100 mL/min. Reaction rate constants for extraction and stripping of Nd(III) were 1.541 and 1.394 min⁻¹. The model developed in this work based on the conservation of mass which consisted of convection, diffusion, reaction and accumulation via HFSLM for the extraction and stripping concentration prediction proved to be in good agreement with the experimental data. Average standard deviations were 1.9% and 1.2% for prediction in feed and stripping sides, respectively. When comparison is made with other models, the model employed in this work rigorously approaches the

experimental data more than the others, implying that the combination of parameters of convection, diffusion and reaction is crucial for accurate prediction in this unsteady state model. The authors claimed that the conservation of mass which consisted of convection, diffusion, reaction and accumulation are very important factors in controlling the rate of transport of Nd(III) along the hollow fibers.

For liquid–liquid membrane extraction, porous membranes are often used due to the lower mass transfer resistance compared to dense membranes. However, in the first case, a rigorous pressure control is necessary to avoid disruption of the interface, and partially soluble extractants (as for example, primary amines) cannot be used. To overcome eventual limitations of mass transfer in dense membranes, an appropriate swelling may be promoted, in addition to a reduction in the membrane thickness. The extraction of solutes in liquid– liquid systems using dense membranes is feasible, but the choice of a solvent with a good interaction with the membrane material is important. In this direction, extraction of succinic acid with five different extractants was accomplished using a membrane contactor fabricated with non-porous cellulose diacetate membrane (dense membrane) [70]. Liquid–liquid extraction tests indicated that the influence of temperature on the distribution coefficients leads to different behaviors when 1-octanol and amines are compared. Primene JM-T1 amine was the best succinic acid extractant among those evaluated, removing 86.0% of the succinic acid in a 0.17 mol/L aqueous solution. For membrane contactor extraction, 45% of acid recovery was achieved, using water as re-extraction agent. This value can be improved, especially for Primene JM-T1 amine, by using a sodium solution in re-extraction or by changing the temperature. Results presented by authors in this work indicated that extraction with non-porous membrane contactor for succinic acid extraction was feasible and advantageous since there are fewer restrictions in the extractant choice.

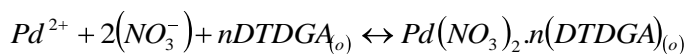
Membrane contactor based technology is also proved to be cost-effective technology and is therefore used to supplant or replace other technologies that may or may not be membrane based. In some situations, membrane contacting has emerged as an enabling technology that is filling certain previously unmet commercial needs. The recent proposals to use hollow-fiber contactors in space missions to recycle waste water or as an artificial lung for patients afflicted with different lung diseases have opened a new horizon for this technology [71].

The use of mixtures of extractants (mainly a solvation extractant plus another type of reagent) improves the extraction rate and the range of pH values in which $\text{Au}(\text{CN})_2^-$ can be effectively transported [72-73]. In this case, the used membrane technology was non-dispersive solvent extraction with one hollow fiber module and it was demonstrated that the use of a LIX 79+TOPO mixture improves the rate of the precious metal recovery (more than 95 % gold from a feed phase of pH 10.3) over six times faster than when LIX 79 (a guanidine derivative) was used alone. These proposed extractant mixtures also improved the $\text{Au}(\text{CN})_2^-$ selectivity over other metal-cyano complexes, i.e. $\text{Zn}(\text{CN})_4^{2-}$, $\text{Ag}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_4^{3-}$, etc., if present in the cyanide solution.

The next paper deals with micro-fibers which can absorb up to seven times its weight in fluids. Micro-fibers are also extremely durable. In this study, the transport of yttrium (III) ions through micro-fiber supported liquid membranes in two stage processes namely source to membrane and membrane to receiving phase was examined by Gaikwad et al,

[74]. The supported liquid membrane was impregnated with different concentrations of carrier, PC - 88A, in toluene. The transport of yttrium (III) ions depended on the pH variation of the source phase; the permeability of yttrium (III) increased with increase in the pH from 1 to 6.5. The PC-88A concentration was also an important parameter in the transport of the metal ion: an increase in the PC - 88A concentration increased the permeability value in the concentration range from 10^{-3} to 0.01 mol/L. Two channels fibers supported liquid membrane solvent extraction enhanced the yttrium transport in comparison with that of single channel fibers supported liquid membrane configuration. The enrichment factor (EF is a ratio of yttrium ion concentrations at time in the receiving to source phase through membrane phase in a continuous process) with respect to initial yttrium ion concentration in source solution decreased with increase in the initial yttrium ion concentration in the source phase. Thus the pre-concentration of yttrium ion is more effective from low concentration solution. Although the author is claiming that the capillary action phenomenon was more effective in the supported fibers liquid membrane but more practical experience is required to establish its performance and repeated use of fibers in experiments.

In recent study performed by Panja et. al.[75], a ligand, namely, N,N,N',N'-tetra-(2-ethylhexyl) dithiodiglycolamide (DTDGA) has been explored as a carrier across a supported liquid membrane (SLM) to study the transport behavior of Pd(II) from nitric acid medium. Extractability and selectivity of Pd (II) has been enhanced over their previously reported extractant, T (2EH) TDGA by introducing a second 'S' atom in DTDGA [76]. Almost quantitative transport of Pd (II) was observed in 2 h time interval using 0.025M DTDGA in n-dodecane as carrier from 4.0MHNO₃ feed solution with 0.01M thiourea in 0.2MHNO₃ as strippant.



Some SLM experiments are performed with HLW diluted solution. HLW solution used for the study had the following composition: U-7.54 g/L, Pu-3.12 mg/L, ¹³⁷Cs-8.94 Ci/L, ¹⁰⁶Ru-7.01 Ci/L, ¹⁴⁴Ce-28.17 Ci/L, ⁹⁰Sr-3.26 Ci/L, ⁹⁵Zr-0.3 Ci/L. From the **Fig. 9** it is evident that none of the elements present in the system were transported to any significant level in the strip phase indicating excellent decontamination factor (DF) of the elements with respect to Pd(II) over 120 min of operation. The Pd (II) transport during the time interval was observed to be >99%. Hence, DTDGA offers an excellent possibility to separate Pd (II) from HLW with excellent DF over other fission products in SLM mode of operation. During 2h time interval almost negligible transport of other fission products present in high level waste (HLW) solution was observed. Various parameters were optimized to achieve maximum transport rate viz., feed acidity, DTDGA concentration in membrane phase, membrane porosity etc. When DTDGA concentration was increased from 0.025M to 0.05M, viscosity of the membrane phase also increases. As the transport of metal ion across a SLM is governed by Stokes-Einstein equation (being diffusion controlled): $D_o = kT/6\pi R\eta$

where D_0 is the diffusion-coefficient, k is the Boltzmann constant, T is the absolute temperature (K), R is the ionic radius (\AA) of solute and η is the viscosity of the medium. As evident from this equation, D is inversely proportional to η , viscosity of the medium (organic solution). So with increasing DTDGA concentration from 0.025M to 0.05 M the membrane transport was slowed down. So 0.025M DTDGA was chosen as the optimum concentration in the membrane phase during these studies. Highest permeability co-efficient value of 2.37×10^{-3} cm/s was observed for 0.025M DTDGA as carrier keeping the feed acidity at 4M HNO_3 and using 0.2 mm PTFE as membrane support. Stability of the membrane was found to be satisfactory by authors over six cycles of operation indicating efficient liquid membrane system can be operated using DTDGA as carrier for selective recovery of Pd(II) from high level waste solution.

3.2. Pseudo emulsion based hollow fiber strip/feed/organic dispersion

In latest advances in PEHFSD, besides the investigation of removal efficiency and enrichment performance, the analysis of mass transfer mechanism of LM is also necessary for the future industrialization. The distribution of mass transfer resistances of HFSD for the removal and recovery of solute was estimated, and the results indicated that the extraction reaction resistance, i.e., the complexation reaction of solute with extractant, generally was dominant [19]. In order to decrease this resistance, a possible approach is to enlarge the mass transfer surface area between the feed and organic phases. As this mass transfer surface area in HDFD locates on the inner surface of hollow fibers, this would suggest that this area can be augmented by increasing the number of hollow fibers. But this would enlarge the size or number of hollow-fiber membrane modules and the amount of organic phase, resulting in an increase of the cost. In addition, from the environmental and economic perspectives, the amount of organic phase should be limited. Actually, in the solvent extraction and HFRLM techniques, the mass transfer area can be greatly increased by dispersing the organic solution in the aqueous solution. In a HFRLM technique, the dispersion flowed through the lumen side of HFM, and the organic-to-aqueous volume ratio was normally less than 1:10, which enhanced the mass transfer performance. Hence, this concept is coupled in recently conducted pertraction studies by Wo et al. [77,78] through supported liquid membranes with feed dispersion (SLM-FD) and supported liquid membranes with organic dispersion has been proposed and studied for simultaneous removal and recovery of Cephalexin from aqueous solutions using a commercially available hollow-fiber module and the carrier Aliquat336 [77,78]. The SLM-FD technique is shown schematically in Fig. 10(a), which has a similar two-phase flow pattern with the SLM-SD or PEHFSD process. Similarly, The SLM-OD technique is illustrated schematically in Fig. 10(b). Under SLM-FD category, various parameters were investigated including the feed-to-organic volume ratio, initial Cephalexin concentration, Aliquat336 concentration in the organic membrane solution, KCl concentration in the strip phase, shell side feed- dispersion flow rate, and lumen side strip-solution flow rate. A comparison of the SLM-FD process with the solvent extraction process was performed, and the results are shown in Fig. 11. The advantage of SLM-FD vs. the solvent extraction process is due to the fact that the former coupled extraction and strip processes simultaneously, resulting in the effective removal and recovery of Cephalexin at the same time. With the increase of Aliquat336 concentration, the mass transfer performance of SLM-FD was enhanced. For the pseudo-steady state, a mathematical model was developed to describe the process. Based on this model, both the theoretical and experimental overall mass transfer coefficients (K_{theo} and K_{exp}) were obtained as a function of Aliquat336 concentration.

These mass transfer coefficients agreed reasonably well. This result indicated that the mass transfer resistance of extraction reaction could be greatly reduced in the SLM-FD process. In addition, the SLM-FD was shown to be superior to the solvent extraction process in terms of Cephalexin removal from the feed solution. In continuation of the same study, supported liquid membranes with organic dispersion (SLM-OD) [refer **Fig. 10b** for more details of SLM-OD] was proposed [78] and investigated for simultaneous removal and recovery of Cephalexin from aqueous solutions by using the carrier Aliquat336 and a commercially available hollow-fiber module (HFM). The effect of KCl concentration on the mass transfer performance is shown in **Fig. 12**. The up-hill mass transfer phenomenon can even be found even with the absence of KCl in the strip phase. **Fig.13** displays the profiles of Cephalexin concentration in the feed and strip phases by varying the lumen-side and shell-side flow rates. When the shell-side (organic dispersion) flow rate was fixed at 200ml/min, by increasing the lumen-side flow rate of the stripping solution from 200ml/min to 400ml/min, the mass transfer performance was not significantly influenced. The results showed that the optimal operating parameters for the removal and recovery of 8mM Cephalexin were 2.5wt% of Aliquat336 concentration, 1M of KCl concentration, and 80:500 of organic-to-feed volume ratio. The authors claimed that the extraction reaction resistance was greatly reduced, amounting to less than 18.3% of the total resistance. This value was much lower than the extraction reaction resistance for SLM-SD (larger than 95%). This technique has limitation when extractants (like primary amines) has more aqueous solubility specially when large O/A ratios are applied in forming aqueous-organic dispersions.

In next study, both solvent extraction and supported liquid membrane process are compared for removing/recovering cadmium from wastewater by Rathore et al. using Cyanex 923 as an extractant/carrier [79]. The influence of acid and chloride ion concentration (neutral and acidic chloride media) on the extraction of Cd (II) was studied. The limiting organic concentration (LOC) values decreased with an increase in the concentration of H^+ . The transport of Cd(II) through flat sheet SLM (FSSLM) was diminished in acidic chloride medium due to appearance of a third phase in the pores of polymeric support. This could be avoided by using an aromatic diluents e.g. Solvesso 200 or by keeping the concentration of metal ions below than the LOC. The influence of Cd (II) concentration and pore size of polymeric support on permeation was found to be negligible through FSSLM in neutral chloride medium, whereas permeation was found to be linearly dependent on the carrier concentration. Although the third phase appeared in acidic chloride medium, the rate of transport of Cd (II) was faster than in the neutral chloride medium with the hollow fiber strip dispersion (HFSD) system. This configuration was found to be rapid with stable life. Results obtained from this study provide improved insights into the HFSD system for the clean-up of cadmium contaminated streams. Hence, author have demonstrated that it was possible to utilize this technique for separation/recovery of Cd(II) from neutral as well as acidic chloride medium using an aliphatic diluent and water as a stripping phase from waste effluent.

In another study, phenol removal from waste waters was examined with different approach through gas-filled membrane extraction technique using hydrophobic membrane contactors by Hasanoğlu [80]. As illustrated in **Fig. 14**, phenol molecules diffuse through the boundary layer to the membrane interface, evaporate at the air filled pore, diffuse through the air-filled pore and then into the strip solution in order to react immediately with NaOH molecules in the stripping side. Hydrodynamic conditions through the membrane contactors in ELM systems are evaluated and it is found

that the mass transfer is dominated by feed side boundary layer resistance however is contributed by both feed side and organic side boundary layer resistances. The experimental overall mass transfer coefficient can be determined from the **equation 1** given below [80]:

$$\ln\left(\frac{C_a}{C_a^0}\right) = -\left(\frac{K_{ov}A + \alpha}{V_{F,0}}\right)t \quad (1)$$

Where $V_{F,0}$ is the initial feed volume, α is the average rate of water vapor transfer and t is the time, K_{ov} of the gas membrane applications can be calculated from the slope of the line obtained by plotting $\ln\left(\frac{C_a^0}{C_a}\right)$ versus t .

Overall mass transfer coefficient for a countercurrent flow where an aqueous and organic phase flow together and the organic phase soaks the pores, can be determined experimentally from **Eq.2**.

$$C_a = \frac{VC_a^o}{1+V} + \frac{C_a^0}{1+V} \exp(-c't) \quad (2)$$

Where c' and related parameters are given below:

$$c' = \frac{Q_a(1+V)}{V_a} \left[\frac{1 - \exp[\phi(\theta-1)]}{1 - \theta \exp[\phi(\theta-1)]} \right] \quad (3)$$

and

$$V = \frac{V_a}{V_o D}, \quad \theta = \frac{Q_a}{Q_o D}, \quad \phi = \frac{AK_{ov}}{Q_a}$$

If the **Eq. (2)** is written as shown in **Eq. (4)** and a graph is plotted between $\ln\left(C_a - \frac{VC_a^0}{1+V}\right)$ and t , the slope of the

straight region of the line will give c' , then the K_{ov} can be calculated.

$$\ln\left(C_a - \frac{VC_a^0}{1+V}\right) = \ln\left(\frac{C_a^0}{1+V}\right) - C't \quad (4)$$

By combining several operations as extraction, stripping and reaction in one unit, it reduces equipment costs and solvent consumption. By emulsion pertraction up to 99.4% of phenol could be removed and 84.6% of the removed phenol could be recovered in the stripping phase.

The next paper deals with cobalt which is used in a wide number of industries. Its re-use possibilities are of paramount interest specially recovery from the wastes generated by the industries. In this direction, transport of cobalt (II) from acidic sulphate solutions through PEHFSD was investigated by Alguacil et al. using the extractant DP-8R in Exxsol D100 [81]. In PEHFSD set-up, the aqueous strip (sulphuric acid) solution was dispersed in the organic membrane solution in a reservoir tank with an impeller stirrer to form a strip dispersion. Several hydrodynamic and chemical parameters, such as variation in feed pH (3–7), cobalt concentration in feed ($0.17\text{--}1.7 \times 10^{-3}$ M), carrier concentration (0.16–1.28 M), etc., were investigated. From experimental data it can be concluded that experimental conditions, i.e. using a pseudo-emulsion phase of 0.64 M DP-8R in Exxsol D100 and 0.1 M H_2SO_4 are suitable for the efficient extraction (higher than 98%) and stripping (higher than 70%) and concentration of Co(II) under optimum operational conditions of i.e. pH of feed phase above 5.0. On the other hand, separation of Co (II)/Li (I) with the required purity ($\beta_{\text{Co/Li}}$ around 25) is possible. As can be seen in **Table 3**, the performance of the system is better than when using Acorga PT5050 or Cyanex 272 as carriers, whereas Co(II)/Li(I) separation factors are similar in the case of DP-8R and Acorga PT5050 extractants and higher than in the case of Cyanex 272. Pilot or large scale studies are needed by authors to work with real solutions from industry to establish feasibility of this technique for cobalt recovery. The quality of cobalt recovered from waste should meet standard specification for further use.

With respect to the toxicity of mercury, it is well known that it has high tendency for binding to the proteins containing thiol and sulfhydryl groups resulting in altered protein synthesis. The long term exposure of mercury causes brain damage, chromosome breakage and dysfunction of liver, kidney, and central nervous system [82]. The trace level concentration of mercury is therefore mandatory to remove from waste streams. For this, pseudo-emulsion hollow fiber strip dispersion system was used in which the pseudo-emulsion phase consisted of di-2-ethylhexylphosphoric acid as a carrier, n-heptane as an organic solvent and sulphuric acid with thiourea as stripping solution [82]. Experiments were carried out in order to optimize the process dependent factors for the maximum extraction of Hg (II) from aqueous solutions of mercuric chloride using face-centered central composite design (CCF). The study has also focused on the effects of various other parameters, such as hydrodynamic conditions, volume ratio of the membrane solution to the stripping solution, stirring speed in the pseudo-emulsion tank. Multiple operations of the extraction using the same strip solution were conducted under optimum process conditions to increase the concentration of mercury in the strip solution and to examine the availability of extraction module for cycling use, which eliminates time and efforts of module cleaning, drying and reassembling. A model developed by regression analysis showed that 98% mercury extraction can be achieved from aqueous solutions at the optimum conditions. With the similar aim of metal recovery, Mondal et al. [83] have investigated the removal rates of vanadium (V) from aqueous solution using PEHFSD technology. A pseudo emulsion was prepared by dispersing hydrochloric acid (stripping) solution into an organic phase constituted of kerosene, Aliquat 336(carrier), and 1-decanol. Within 60 min, typical results with continuous recycling of both the

feed and the pseudo-emulsion employing carrier concentration of 0.025M and feed pH 5 showed that extraction was nearly 99% whereas maximum recovery in the HCl solution achieved was over 85%. Mathematical analysis suggested that the removal rates were controlled by mass transfer resistance from extraction and stripping reactions. The accepted level of vanadium in water supplies and irrigation water is 200 ppb and 10 mg/L, respectively [83]. Compliance to environmental regulations requires the processing of waste water for the removal of the species, to prevent its dissemination to the environment. Therefore above study will help in this situation to remove vanadium contamination from desired stream. In the same vein of continuous improvement, the transport of copper from acidic sulphate solutions using pseudo-emulsion based hollow fibre strip dispersion (PEHFSD) technology was investigated by Agarwal et al. [84]. The aldoxime Acorga M5640 was used as an extractant. The influence of several parameters like the flow rates, the initial concentration of Cu(II), the extractant amount, the pH, the presence of sodium sulphate, the use of a leach solution with Zn(II) and Fe(III) as the feed phase and lean electrolyte as strippant was studied. The analysis was made on the basis of the overall mass transfer coefficient of copper. This coefficient was also estimated by applying the resistance in series approach, the contribution of each resistance to the overall resistance to mass transfer being evaluated. Some experiments with zinc leach solution on emulsion liquid membranes (ELMs) were also conducted to compare the results of ELM and PEHFSD. In another study, Agarwal et al. [85], transport of zinc from sulphate solutions using pseudo-emulsion based hollow fibre strip dispersion technique was investigated. The reagent Ionquest 801 was used as an extractant in most experiments. The influence of several parameters like the flow rates, the initial concentration of Zn (II), the extractant amount, the pH, the volume ratio of feed to strippant, and the presence of Ca (II) in the feed phase was studied. A few tests with the extractants Cyanex 272 and DEHPA were also carried out for comparison. Equilibrium data of zinc and calcium extraction were obtained. The analysis of zinc transport was made on the basis of the overall mass transfer coefficient of permeation. This coefficient was also estimated by applying the resistance in series approach, the contribution of each resistance to the overall resistance to mass transfer being evaluated. Ionquest 801 showed to be a potential carrier of zinc ions in the presence of calcium because of its fast kinetics of permeation and high separation factor Zn/Ca. The use of Cyanex 272 and DEHPA led to less attractive results. Cyanex 272 exhibited a relatively low permeation rate of Zn (II) and the performance of DEHPA was strongly affected in the presence of calcium, the value of KP being particularly reduced for the extraction of Zn (II). The system with Ionquest 801 was also tested on the recovery of zinc from an industrial effluent, the performance of the liquid membrane process being observed very satisfactory.

In order to increase the overall efficiency of the system, mixture of extractants were also examined by researchers. In this direction, the transport of $\text{Au}(\text{CN})_2^-$ between alkaline aqueous solutions and organic phases consisting of a mixture of the amine Primene JMT and the phosphine oxide Cyanex 923 in xylene was studied using the pseudo-emulsion based hollow-fiber strip dispersion (PEHFSD) technology. [86]. The feed phase was passed through the lumen side, and the pseudo-emulsions of the extractant mixtures and NaOH were passed through the shell side in a counter current mode using a single hollow-fiber contactor for extraction and stripping. In this membrane technology, the strippant (NaOH solution) is dispersed in the organic (Primene JMT + Cyanex 923 in xylene) membrane solution in a tank with an impeller

stirrer adequate to form strip dispersion. The pseudo emulsion phase is circulated from the reservoir tank to the membrane contactor to provide a constant supply of the organic solution to the membrane fibers. Furthermore, this technology allows a direct contact between the organic and strip solutions, providing a greater area for stripping and facilitating the metal recovery from the strip solution once both phases are separated. Various hydrodynamic and chemical parameters, such as flow of feed phase, extractant mixtures and gold concentrations, organic diluents, variation in feed pH, and the selectivity of the system with respect to the transport of different metal-cyano complexes, were investigated. Aqueous and membrane mass transfer coefficients were estimated by authors for the present system. The maximum in metal permeation or limiting permeability value could be attributed to a permeation process controlled by the diffusion in the stagnant film of the aqueous feed phase. Thus: $P_{lim} = D_{aq}/d_{aq}$ and assuming a value of D_{aq} (aqueous diffusion coefficient) in the order of 10^{-5} cm²/s, then the thickness of the aqueous boundary layer (d_{aq}) was estimated as 6.7×10^{-2} cm. Under this limiting condition, $P_{lim} = k_f = 1.5 \times 10^{-4}$ cm/s. The decrease of metal permeation at the highest extractant mixture concentration could be attributed to an increase in the organic-phase viscosity which reduced the diffusion coefficient and increases the membrane resistance.

In another application, a double strip dispersion hybrid liquid membrane (SDHLM) was successfully used in the simultaneous extraction and separation of Cu (II), Zn (II), and Co (II) from Cu-Zn-Co dilute feed phase by Luo et al [87]. **Fig. 15** shows the scheme of the strip dispersion hybrid liquid membrane used for this study. The effect of the different experimental variables on separation was examined. The optimum separation conditions were summarized. Dodecanol was added as a modifier for the membrane stability. **Figure 16** shows that dodecanol is beneficial to the transport of Zn (II) ions, but dodecanol in membrane hinders the transport of Cu (II) ions. In the later experiments, the concentration of dodecanol in the membrane was 0.24M for Zn(II) and no dodecanol was added in the membrane for Cu(II). **Figure 17** indicates that the mass transfer coefficient of zinc (II) ions increases with an increase of x up to x=10:110=0.091 and beyond x=10:110 the mass transfer coefficient decreases. For the transport of Cu(II), the mass transfer coefficient of Cu(II) increases with an increase of x up to x=20:100=0.20 and beyond x=20:100 the mass transfer coefficient decreases. When x increases, the droplets of the aqueous strip solution dispersed in the organic phase obviously increase and the membrane thins out. Results indicated that the optimum volume ratio for the transport of Zn²⁺ and Cu²⁺ is 10:110 and 20:100, respectively. An analysis of mass transfer resistances in the double SDHLM system showed that the mass transfer resistance for the diffusion of Zn (II) ions in the micro porous membrane phase is dominant and the mass transfer resistances for the diffusion of copper (II) ions in the aqueous boundary layer and in the micro porous membrane phase are dominant in comparison with the overall mass transfer resistance. In this study, more work is required in this field in order to approach more practical separation problems in order to establish SDHLM for large scale applications.

In a recent paper, Bringas et al. presented computer-based simulation methodology to analyze the advantages of employing concentration driven membrane extraction separation processes based on the combination of reactive liquid membranes and membrane contactors [88]. The important objective was tackled by illustrating the performance of the

scaled up HFSD or EPT process applied to the regeneration of chromium-based passivation baths. In this study, the comparison, through suitable intensification metrics, of conventional solvent extraction and EPT both applied to the recovery of valuable components from the spent pickling solutions generated in the hot-dip galvanizing process has been analyzed. Some of the main conclusion of this study were : (a) the integration of the EPT process in the in situ treatment of a passivation bath (volume = 1.5 m³) with capacity for the continuous removal of zinc and iron at rates of 1.2 kg day⁻¹ and 0.21 kg day⁻¹, has been designed. (b) two different indexes, the productivity/size ratio (PS) and the modularity (M), defined below were selected to evaluate the degree of intensification resulting from the comparison between EPT and a conventional solvent extraction process. The first proposed index, PS, compares the ratio between the productivity and the equipment size for both the membrane units and the conventional operations

PS (Productivity /size ratio) = Productivity/size

$$PS(\text{Productivity /sizeratio}) = \frac{\text{Productivity/Size}_{(\text{membranes})}}{\text{Productivity/Size}_{(\text{traditional})}} \quad (5)$$

To compare the modularity of membrane contactors versus traditional units, the modularity index (M) is defined according to **Eq. (6)**.

$$M(\text{modularity}) = \frac{|A_2 / A_1(\text{membranes}) - \text{productivity}_2 / \text{productivity}_1|}{|V_2 / V_1(\text{traditional}) - \text{productivity}_2 / \text{productivity}_1|} \quad (6)$$

.....

The calculated value of the index PS was 11.7 and modularity index (M) was 0.73, thus confirming the benefits of employing the EPT process versus the conventional technology for scale-up purposes.

3.3. Hollow fiber renewal liquid membrane (HFRLM)

In last few years, researchers are working on hollow fiber renewal liquid membrane (HFRLM) and this technique is being deployed for various applications. This technique is based on the surface renewal theory, and integrates the advantages of fiber membrane extraction, liquid film permeation and other liquid membrane processes [28, 89]. The results from the system of CuSO₄+D2EHPA in kerosene+HCl show that the HFRLM process is very stable. The liquid membrane is renewed constantly during the process, the direct contact of organic droplets and aqueous phase provides large mass transfer area. The overall mass transfer coefficient increases with increasing flow rates and D2EHPA concentration in the organic phase, and with decreasing initial copper concentration in the feed phase. The overall mass transfer coefficient also increases with increasing pH in the feed phase, and reaches a maximum value at pH of 4.44, then decreased. Also, there is a favorable w/o volume ratio of 20:1 to 30:1 for this process. Compared with hollow fiber supported liquid membrane and hollow fiber membrane extraction processes, HFRLM process has a high mass transfer rate. Mathematical model for the HFRLM process based on the surface renewal theory was developed. The calculated

results were in good agreement with experimental results under the conditions studied. Since the transport of copper with D2EHPA as carrier was predominantly governed by aqueous layer diffusion of the feed phase, it is better for the HFRLM processes that the stirred mixture of the feed phase and the organic phase flows through the lumen side of the module. Because of the effect of the mass transfer driving force, caused by distribution equilibrium, the overall mass transfer coefficient increases with increasing D2EHPA concentration in the organic phase and decreases with increasing initial copper (II) concentration in the feed phase. Based on the surface renewal theory, a mathematical model for the HFRLM process was developed. The calculated overall mass transfer coefficients were in good agreement with experimental results. The surface renewal mechanism should be verified by other techniques also and should be tried with various extractants-metal systems.

For drinking water and irrigation uses, the Cl^- must be reduced by conventional water treatment processes, like ion exchange or reverse osmosis, but for large scale production, these techniques could be very expensive due to resin regeneration or energy costs. The possibility of using HFRLM with ionic liquids (IL), Aliquat 336, Cyphos IL 101 and Cyphos IL 167, as carriers to exchange Cl^- for HCO_3^- anion has been investigated [90]. The reversibility of this anion exchange was corroborated by solvent extraction experiments and implemented in flat sheet supported liquid membrane (FSSLM) and hollow fiber renewal liquid membrane technologies (HFRLM) [Fig 18]. About double transport values have been obtained in HFRLM compared to SLM and 1 h is the time enough to reduce the chloride concentration up to 250 mg/L using HFRLM at the best experimental condition. The results obtained indicated the possibility for implementation of this technology on a large scale to chloride reduction in drinking water when the source is inadequate for direct use. Solvent extraction experiments have been designed to obtain equilibrium data and to analyse the equilibrium behaviour. The reversibility of the $\text{Cl}^-/\text{HCO}_3^-$ interchange process has been verified. Chloride anion can be effectively transported through the liquid membranes containing Aliquat 336, Cyphos IL 101 or Cyphos IL 167 as carriers. The chloride reduction efficiency of the process is higher than 80% after 4 h of running at the best working conditions. Renewal ionic liquid membrane technology prevented the organic losses and allowed us to increase the efficiency of the separation. This technique could be also applied to exchange any other anion present in aqueous solutions choosing adequately the counter-ion and the IL. The mass transfer velocity is faster at higher concentrations of Aliquat 336 but this effect is dampened by the rise of the viscosity of liquid membrane. In comparison with the chloride fluxes on SLM membranes these values are bigger as a consequence of the membrane characteristics as the ratio porosity/thickness. The circulation in closed loop along this membrane module (feed–membrane–feed, and emulsion/membrane/emulsion) produces an accumulative effect in the stock tanks. Because of this functioning, after a long operation time the $[\text{Cl}^-]$ in the feed tank achieves a constant value (about 124 mg/L) and the chloride transfer was stopped due to the high content of chloride in the stripping solution (about 4770 mg/L). Author claimed that renewal ionic liquid membrane technology prevented the organic losses and allowed to increase the efficiency of the separation. This technique could be also applied to exchange any other anion present in aqueous solutions choosing adequately the counter-ion and the IL.

In another study, hollow fiber renewal liquid membrane (HFRLM) and hollow fiber supported liquid membrane (HFSLM) were used to simultaneously remove and recover copper(II) from aqueous solutions, and the transport performance of these two techniques were compared under the similar conditions for the system of $\text{CuSO}_4 + \text{D2EHPA}$ in kerosene + HCl [91]. The HFRLM process had a higher overall mass transfer coefficient than that of HFSLM process in single-pass experiments. These were because the renewal effect of the liquid membrane layer could reduce the mass transfer resistance of the lumen side and replenish the loss of the membrane liquid in the HFRLM process. The fractional resistance of the lumen side in the HFRLM process, which was less than 60 percent, was less than that in the HFSLM process, which was higher than 80 percent. At 8 h, the removal efficiency of copper(II) was up to 67.1% in the HFRLM process, the enrichment factor was up to 4.0, which were faster and higher than that of the HFSLM process. Although, the authors have demonstrated that the HFRLM technique was a prospective method of simultaneous removal and recovery of copper from aqueous solution than HFSLM but operation by larger set up will have to be conducted for knowing industrial feasibility. Zhang et al. have used HFRLM to simultaneously remove and recover copper from acidic wastewater [27]. The commercial extractant, LIX984N, was used as a carrier in liquid membrane phase and kerosene used as a diluent. CuSO_4 solutions is used to simulate acidic industrial wastewater, in which the pH is adjusted by dilute H_2SO_4 . The mass transfer mechanism of the process was investigated. The higher pH in the feed phase (>3) and H_2SO_4 concentration in the stripping phase around 2.0 mol L^{-1} are favorable for the transport process due to the increase of mass transfer driving forces. The mass transfer fluxes increase with increasing flow rates on two sides. The countercurrent cascade experiments show that the HFRLM process could carry out the simultaneous removal and recovery of copper from wastewater successfully. The mass transfer fluxes increase with the increasing flow rates on two sides, while the removal efficiency increases with the increasing flow rate on lumen side and decreases with the increasing flow rate on shell side. The mass transfer model based on the surface renewal theory is presented by considering the renewal process of liquid membrane layer, diffusion across membrane phase and aqueous boundary layer on the shell side. The authors demonstrated that HFRLM is a promising method for the treatment of acidic wastewater containing copper and cascade experiments should be tested on pilot level to prove its feasibility for industry.

Recently, most of the studies on liquid membranes have been focused on the simple system with one metal ion component which can not be used to treat complicated solutions directly, because the factors, such as interaction among metal ions, selectivity of liquid membrane phase for different metal ions, etc., have not been considered. Therefore, in next study, extraction separation of Cu (II) and Co (II) from sulfuric wastewater was studied with HFRLM technique [29]. The organic solution of LIX 984N in kerosene was used as the liquid membrane phase to selectively separate and concentrate Cu(II) from aqueous solution; and the extractant CYANEX 272 is used as carrier to remove and concentrate Co (II) from aqueous solution. The removal efficiency of Cu (II) increases with the increasing flow rate on lumen side, while decreases with the increasing flow rate on shell side. The results of lab-scale cascade experiments show that the HFRLM technique is a promising treatment method for simulated sulfuric wastewater containing copper

and cobalt with separation factor higher than 100. The separation factor is higher than 100; and the concentrations of copper and cobalt in the outlet of feed solution is below 0.50 mg L^{-1} and 1.0 mg L^{-1} , respectively.

3.4 Supercritical fluids based membrane extraction (SFME)

The mass transfer in a membrane-based dense gas extraction of metal ions from aqueous solutions using membrane contactor is a novel area and drawing maximum attention in last few years. Several authors are working in this field as can be judged by recent published literature in this field [1-2]. Extractions of Cu (II) were carried out in a single fiber membrane contactor operating under steady state conditions [92]. Aqueous CuSO_4 solutions were treated using a CO_2 phase containing 1, 1, 1-trifluoro-2, 4-pentanedione (TFA) or 1, 1, 1, 5, 5-hexafluoro-2, 4-pentanedione (HFA) at 40°C and pressures ranged between 70 and 90 bar. Experiments showed that the use of dense CO_2 as extraction solvent of Cu (II) ions reached extraction efficiencies valued up to 98.7%. The mass transfer fluxes through the membrane seems to be higher than similar membrane-based extraction processes reported in the literature using organic solvents, since transport properties of the extraction phase are closer to the gas phase. The influence of the acidity of the aqueous solution on the extraction performance could confirm that was required a high content of protons to facilitate and stabilize the formation of a keto-enol tautomerism during the complex formation. From the experimental results and phenomenological equations an effective complex formation rate was estimated at the aqueous- CO_2 interface. This effective kinetic equation allows correlating the transfer of Cu^{2+} through the porous membrane and it could be used as a tool to scale-up this process. Finally authors proposed a novel intensified operation based on this study which could be applied for high valued metals or hazardous materials.

In another study, mass transfer modeling of solvent extraction by means of membrane contactors based on solving conservation equations for solutes in the membrane contactor was investigated by Shirazian et al. [93]. The system considered here was a polymeric membrane contactor, an aqueous solution of ethanol or acetone, and a dense solvent. The equations of the model were solved by numerical method using CFD techniques.

The Reynolds numbers for the range of flow rates considered are between 0.05 and 20. A mathematical model was developed that could calculate the steady state concentration of the solute. Both axial and radial diffusions were considered in the model. Simulation results indicated that the extraction of acetone is higher than ethanol due to higher solubility of acetone in the solvent. The simulation results revealed that decreasing feed velocity and increasing solvent velocity increased solute removal. The developed mass transfer model was more accurate than other models and represented a general approach for simulation of membrane-based solvent extraction. The model findings were compared by authors with the experimental data and showed good agreement for extraction of ethanol and acetone from aqueous solutions.

3.5 Ionic liquid based membrane extraction (ILME)

Since the concept of ILME is quite similar to that of conventional SLMs, it seems logical that the same membrane configurations used in the latter will be useful when ionic liquids are used as carriers in supported membrane operation. Flat-sheet supported liquid membranes (FSSLMs) are useful to obtain first data about the permeation of a given solute. However, for practical purposes, membrane configurations with higher surface area to volume ratio, such as spiral wound and hollow fiber modules are required. In hollow fiber modules, the ionic liquid is confined, by capillarity, within the pores of the hollow fibers, and the aqueous feed and strip solutions circulate by each side of the fiber, thus, the solid membrane serves both as a support for the ionic liquid and as a uniform barrier between the aqueous solutions, which usually circulate within the inner (feed solution) and the outer (strip solution) of the fiber. This results in two aqueous/ionic liquid interfaces with well defined transfer areas.

In these type of configuration with ionic liquid, the permeation of chromium (III) using PEHFSD technology and the ionic liquid ($RNH_3^+HSO_4^-$), formed by reaction of the primary amine PRIMENE JMT and sulphuric acid, dissolved in n-decane as mobile carrier was investigated by Alguacil et al. [94]. The alkaline feed solution containing Cr(III) was passed through the tube side, and pseudo-emulsions of the ionic liquid + n-decane + n-decanol and sulphuric acid were passed through the shell side in counter-current mode and using a single hollow fiber module for extraction and stripping. The overall mass transfer coefficient was calculated by following equation:

$$\ln\left(\frac{[Cr]_t}{[Cr]_o}\right) = -\frac{A}{V_f} K_t$$

Where, V_f is the volume of the feed solution, A is the effective membrane area in the module, $[Cr]_t$ and $[Cr]_o$ are the chromium concentrations in the feed solution at an elapsed time and time zero, respectively, and t is the time.

On the other hand, and under certain experimental conditions (i.e. at shorter transport times or under complete solute-loading of the carrier), the membrane flux was calculated by:

$$[Cr]_t - [Cr]_o = [RNH_3^+HSO_4] K_m \frac{A_t}{V_f}$$

where k_m is defined as the membrane mass transfer coefficient. In this situation, the flux is constant with time and plotting $[Cr]_t$ versus time, a straight line was obtained and therefore it was possible to calculate D_{org} . The slope value of this straight line can be correlated to an initial mass transfer coefficient, K_o , defined as:

$$K_o = \frac{J}{[Cr]_o} = \left[[RNH_3^+HSO_4] \frac{K_m}{[Cr]_o} \right]$$

In this advanced membrane technology, the aqueous acidic strip solution is dispersed in the organic membrane solution in a tank with an impeller stirrer to form a strip dispersion. The pseudo emulsion phase is circulated from the tank to the

membrane module to provide a constant supply of the organic solution to the membrane micro pores. Factors affecting chromium permeability, such as hydrodynamic conditions, carrier concentration in the organic phase, metal and NaOH concentrations in the feed phase, have been analyzed. A model was reported describing the transport mechanism, whereas the experimental data were quantitatively explained by mathematical equations describing the rate of transport.

In another approach, stabilization of a room temperature methylimidazolium cation based ionic liquid (IL) into the pores of ceramic nanofiltration (NF) membranes was achieved by means of a novel in-situ, pressure assisted imbibition/reaction method [95]. From the results, authors have concluded that the longer alkyl chain of the silane molecule (propyl chloro, instead of methyl chloro silane) was not sufficient to provoke the complete blockage of the 5 nm pores (SILM5B)[$C_{10}H_{21}N_2SiO_3PF_6$, pore size 5 nm]. The propyl chain was long enough to prohibit the entrance of the silylated-IL (1-methyl-3-(3-trimethoxysilylpropyl) imidazolium hexafluorophosphate) into the 1 nm pores of membrane SILM1C [$C_{10}H_{21}N_2SiO_3PF_6$, pore size 1 nm]. In this case, the permeability was about one order of magnitude lower than this of the unmodified membrane as a consequence of the deposition of the silylated IL molecules on the external surface of the top-separating layer, around the pore mouths. Thus the pore mouth openings were partially blocked resulting to considerable hindrance on the entrance of the gas molecules into the pore structure but not to a considerable enhancement of the CO_2/CO selectivity since the deposited IL phase was not exerting full control over the diffusion of the gaseous molecules. The CO_2/CO separation performance of the modified membranes was quite significant. The maximum CO_2/CO separation factors achieved were 11 at 30 °C, 25 at 50 °C, 12 at 100°C and 5 at 230°C. The respective CO_2 permeability values were 226, 520, 715 and 2000 Barrer. The stability of the developed membranes has been verified, in 3 sequential cycles of heating/cooling, in the temperature range between 25 and 250°C and under a differential pressure up to 0.5 MPa.

Applications of ILs and/or TSILs in the removal of metals using supported liquid membrane technologies are very rare; the use of some of these reagents in the separation of metals and has been recently reported in the literature [39,44]. Rios et al. [96] have examined a wide range of ionic liquids with different cation and anion compositions liquid phase in supported liquid membranes. It was found that selectivity values are mostly dependent on the anion composition of the ionic liquid, the highest value being reached with ionic liquids based on the methylsulfate anion. With regard to cation composition, it was observed that higher selectivities were reached with ionic liquids which contain cations with shorter alkyl chain lengths. Furthermore, a relationship was established by authors between the permeability of the compounds and their hydrophilicity based on Hildebrand solubility parameter of each compound.

In another publication of same author, solute transport was analyzed by the permeability parameter (\bar{P}) and transport model for the calculation of this parameter was described in detail [97]. In brief, no concentration polarization conditions at the membrane interfaces and no accumulation of the solutes in the membrane and liquid films have been

considered. Under these hypotheses, the permeability can be calculated using Eq. (7), from the slope of the plot of $\ln[(C_0 - 2C_r)/C_0]$ versus t :

$$\ln\left[\frac{(C_0 - 2C_r)}{C_0} = \frac{-2\bar{P}A}{V}t\right] \quad \dots 7$$

Where C_0 is initial solute concentration in the feed phase (mol L^{-1}), C_r is the solute concentration in the receiving phase (mol L^{-1}), A is the membrane area (cm^2) and V is the volume of the compartments (mL). \bar{P} values were reported with a relative standard deviation of 3% or less.

Furthermore, the average permselectivity ($r\bar{P}$) of the membrane was determined as a numerical criterion to compare the ability of the different membranes to separate the target compounds **Eq. (8) . [97]**

$$r\bar{P} = \sum_i^n \frac{rP_i}{n} \quad \text{with } rP_i > 1 \quad \dots\dots 8$$

Where rP_i is the membrane permselectivity between two compounds (e.g. 1-butanol and vinyl butyrate) and n is the number of possible pairs of different compounds. rP_i can be expressed as follows:

$$r\bar{P}_i = \frac{\bar{P}_A}{\bar{P}_B}$$

This parameter indicates the efficiency of the membrane in separating the compounds: the higher $r\bar{P}$, the more selective it is in separating the target compounds. In this study authors have also outlined the possibility of tailoring ionic liquids for use as extraction agents immobilized in supported liquid membranes for application in the selective separation of the substrates and products of a transesterification reaction. The anion composition of the ionic liquid was seen to strongly influence the selectivity of the separation, the highest value being reached with the ionic liquid containing the methylsulfate anion. It was also found that dialkylimidazolium cations led to higher selectivity than alkyipyridinium cations. Furthermore, an increase in the selectivity values was observed with the decrease in the alkyl chain length of the substituent in the imidazolium ring. The molecular mechanism involved in the transport phenomena through the SLMs was also investigated by determining the partition coefficients of the different compounds between n -hexane and the ionic liquids. It was concluded by authors that transport was mainly regulated by the ionic liquid's

affinity towards each solute, which can be assessed simply by evaluating the Hildebrand solubility parameter of each compound.

To capture carbon dioxide directly from ambient air, the fabrication of supported ionic liquid membranes (SILMs) on asymmetric and symmetric micro porous poly (vinylidene fluoride) (PVDF) membranes were studied [98]. The effect of support membrane structure on the IL loading, the stability of fabricated SILMs, and the carbon dioxide (CO₂) capturing abilities of both SILMs were evaluated. The evaluations include the gas permeation of pure CO₂ and nitrogen (N₂), the mixed CO₂-N₂ gases containing 50%, 10% and 1% CO₂, and the directly compressed ambient air. The results demonstrated that pure CO₂ showed the highest permeance, followed by CO₂-air and then N₂. Compared with asymmetric SILMs which had higher gas permeance, the symmetric SILMs had better selectivity for CO₂/N₂, to more than 20 of CO₂/N₂ selectivity, for both single and mixed gases. The SILMs also were found to be capable of capturing CO₂ from air from 2 to more than 5 of CO₂/air selectivity for separation of air enriched with low CO₂ concentrations (10%, 1% and zero) as the transmembrane pressure increased to 0.25 MPa. Thus, this work might provide a potential method for sequestering CO₂ directly from atmosphere to avoid the need for extensive CO₂-transportation.

In another work, performance of ionic liquid in supported liquid membrane (SLM) for the removal of phenol from waste water was evaluated by Nosrati et al. [99]. In this work, 1-n-alkyl-3-methylimidazolium salts, [C_nMIM]⁺[X]⁻ have been investigated so as to determine an optimal supported ionic liquid membrane. It was demonstrated by authors that up to 85 percent of phenol can be removed from wastewater by using the ionic liquid [BMIM][HSO₄] with PTFE membrane filter. A stable SILM comprising of [BMIM][HSO₄] and the hydrophobic PTFE support was achieved for over the experimental run of more than 24 h. Although, NaOH concentration was not a significant parameter, it was required as the stripping agent to remove phenol efficiently.

It is already known that stability is the principal limitation in deploying SLM for industrial applications. Liquid membrane solubility in aqueous phases, wetting of the support pores, osmotic pressure gradient or pressure difference over the membrane, shear induced phenomena and blockage of the pores are proposed by different researchers as the SLM instability mechanisms [100-102]. However, these mechanisms are not in the same level of influence and significance. Osmotic pressure mechanism is a controversial mechanism. According to Fabiani et al. [103] and Danesi et al. [104], osmotic pressure gradient could reduce the stability of the SLM, but the idea was first challenged by Neplenbroek et al. [105]. He explained that by an increase in osmotic pressure SLM stability improves and the water transport is not a reason but a cause of SLM instability and that is in contrast to the osmotic pressure mechanism. In the instability investigation for removal of phenol by Zha et al. [106] the same result was obtained and they claimed that the osmotic pressure difference was not the cause of SLM degradation. Moreover, in a recent research on phenol removal by Zheng et al. [107], the mechanisms of solubility and osmotic pressure are proved not to be important instability mechanism, although they are also contributed to the loss of membrane liquid. Emulsification is claimed to be the main mechanism of instability [101, 106, 107]. To improve the stability it is suggested to choose: low stirring speed, supports with smaller pore size and high hydrophobicity and also to reduce the factors which are favorable for the formation of emulsions

such as high HLB (hydrophile–lipophile balance) value or water solubility [100,104, 105,]. In this study, a hydrophobic support with small pores was chosen. The membrane phase only contained ionic liquid and no surfactant was added. In the experiment with ionic liquid [BMIM][HSO₄], no sodium phenolate was detected in the feed side for over the experimental run of more than 24 h and no proton leakage was observed in this time. Imidazolium cation was detected in the feed phase at the same time of phenolate detection. It can be attributed to the membrane solubility. Further investigation must be done to determine the dominant mechanism in the supported ionic liquid membrane systems.

In continuation of SILM research, SILMs were prepared with the room temperature ionic liquid (RTIL) 1-hexyl-3-methylimidazoliumchloride ([hmim][Cl]) and the cuprous chloride (CuCl) copper (I) salt to perform the selective separation of CO from N₂[108]. Previously, authors reported that this solute-carrier system provides large CO/N₂ solubility selectivity due to the reversible formation of a CO–copper(I) complex. The RTIL was impregnated in a porous PVDF membrane and pure and mixed gas permeation experiments were performed with continuous gas flow at constant pressure. The effects of different operating conditions were tested, namely pressure, temperature, sweep gas flow rate and liquid membrane composition. The CO permeability through the copper (I)-based SILMs increased with respect to pure [hmim][Cl]–SILMs owing to the CO carrier-mediate transport. On the contrary, the N₂ flux is not affected, and therefore, the CO/N₂ selectivity was increased. The CO transport through the reactive SILMs is enhanced at higher temperature and copper (I) concentration. However, mixed gas experiments revealed a slight decrease of CO/N₂ selectivity. Regarding membrane stability, SILMs were continuously operated for two weeks without any loss of performance. Additionally, gas diffusion coefficients ($\sim 10^{-10} \text{m}^2 \text{s}^{-1}$) and solute-carrier complex diffusivity ($\sim 10^{-11} \text{m}^2 \text{s}^{-1}$) were calculated in the RTIL media.

A method to predict the gas permeability of supported ionic liquid membranes (SILMs) was established, using as input the pore structure characteristics of asymmetric ceramic membrane supports and the physicochemical properties of the bulk ionic liquid (IL) phase [109]. The method was applied to investigate the effect of IL nano confinement on the CO₂ and N₂ permeability/selectivity properties of novel SILMs developed on nano filtration (NF) membranes employing for the first time the 1-ethyl-3-methylimidazolium and the 1-butyl-3-methylimidazolium tricyanomethanide ILs as pore modifiers. The selected ILs exhibit low viscosity, which allows for faster gas solvation rates and ease of synthesis/purification that makes them attractive for large-scale production. In parallel, the use of ceramic supports instead of polymeric ones presents the advantage of operation at elevated temperatures and pressures and offers the possibility to study the “real” permeability of the confined IL phase, avoiding additional contributions from the gas diffusion through the surrounding solid matrix. The developed SILMs exhibited enhanced CO₂ permeability together with high CO₂/N₂ separation capacity, though with distinct variations depending on the alkyl chain length of the 1-alkyl-3-methylimidazolium cation. Application of the developed methodology allowed discriminating the contribution of the NF pore structural characteristics on the SILM performance and unveiled the subtle interplay of diverse IL confinement effects on the gas permeability stemming from the specific layering of ion pairs on the nano porous surface and the phase transition of the IL at room temperature, dictated by small variations of the IL cation size.

In another study, authors fabricated polyethersulfone (PES) hollow fibers via stable core annular flow in a coaxial microfluidic device. By adjusting the dope solution composition, hollow fibers with finger like micro voids as well as macro void-free hollow fibers were successfully prepared [110]. Different RTILs were immobilized in the produced hollow fibers for CO₂-N₂ separation. The formed supported ionic liquid membranes were stable under a working pressure difference of 0.7 bar. The effect of permeate direction on the pure gas permeability and idea selectivity was studied. A higher CO₂ permeability and CO₂/N₂ selectivity was obtained when the gas permeated from the shell side to the tube side, as compared with that when the gas permeated from the tube side to the shell side. The effect of the support structure on the membrane performance was also investigated, and the results showed that the existence of fingerlike macro voids increased the CO₂ permeability and decreased the CO₂/N₂ selectivity. Most of the results presented by authors in this study were close to the Robeson upper bound and suggested that the SILMs produced in this work were highly selective for CO₂ separation. This study also showed that the hollow fiber membrane could also be a more promising support material for SILMs than a flat sheet membrane.

In the similar line, another study was focused on the permeability modulation of supported magnetic ionic liquid membranes (SMILMs) for CO₂ separation, when applying an external magnetic field [111]. Four magnetic ionic liquids (MILs) have been studied ([P₆₆₆₁₄][CoCl₄], [P₆₆₆₁₄][FeCl₄], [P₆₆₆₁₄][MnCl₄] and [P₆₆₆₁₄][GdCl₆]) in combination with a commercial hydrophobic PVDF porous support. An experimental evaluation of the membrane permeability was carried out for CO₂, N₂ and air. The influence of the magnetic field on MILs viscosity was also studied, allowing to establish the relationship between permeability and viscosity depending on the external magnetic field. An external magnetic field between 0 and 2T increases the gas permeability for CO₂, N₂ and air without changing the permeability ratio and decreases MILs viscosity, depending on the MILs magnetic susceptibility. The MIL [P₆₆₆₁₄][GdCl₆] shows the maximum CO₂ permeability increase (21.64%) in comparison with the result when no magnetic field is applied. The permeability and viscosity product is a constant with a different value for each SMILM studied. Experimental results confirm the potential for gas permeability modulation through supported liquid membranes by tuning the external magnetic field intensity.

Room temperature ionic liquids are emerging as alternative solvents which replace the conventional volatile organic solvents. The solvent extraction/liquid membrane process requires substantial amount of solvent as well as stripping of solute from the solvent. In another study, Santos et al. [112] have prepared SILMs with the acetate based RTILs, 1-ethyl-3-methylimidazoliumacetate ([Emim] [Ac]), 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) and the monomer vinylbenzyltrimethylammoniumacetate ([Vbtma] [Ac]) in order to perform the selective separation of carbon dioxide (CO₂) from nitrogen (N₂). The RTILs were supported in a polyvinylidene fluoride porous membrane and permeation experiments were performed in the temperature range 298–333K. Gas permeability increased with temperature while an increase in temperature leads to a decrease in the CO₂/N₂ selectivity for all the studied RTILs. CO₂ solubility was evaluated in the range 298–333 K and atmospheric pressure using thermo gravimetric techniques. Diffusion coefficients were calculated based on the solution–diffusion theory using gas permeability and solubility data. The temperature influence on the gas permeability, solubility and diffusivity are well described in terms of the Arrhenius–van't Hoff

exponential relationships. In this work, CO₂ and N₂ permeability through SILMs were determined at temperatures ranging from 298 to 333K. Gas permeability increased with the temperature while CO₂/N₂ selectivity decreased with an increase in temperature for all the studied RTILs. The permeability activation energies are higher for nitrogen than for carbon dioxide. Acetate based SILMs are useful for CO₂/N₂ separation since the results obtained in this work are near the Robeson upper bound corresponding to the best polymeric materials. Gas diffusion coefficients were estimated as summing that gas permeation occurs via a solution–diffusion mechanism (P=DS) and the activation energies for the permeability, solubility and diffusivity were calculated. The experimental results of the activation energies and the absorption enthalpies agreed well with the previous literature results. In order to get a higher influence of the temperature in the permeability, it is recommended by authors the introduction of RTILs with an endothermic absorption, which may increase the permeability activation energy.

In another work, the extraction of Cu (II) using quaternary ammonium and quaternary phosphonium based ionic liquids [113] was investigated. Firstly, the chemical suitability of the two ionic liquids was evaluated. They were then tested for extracting copper from solutions (simulated) of liquid mining waste. The effects of the extractant concentration, the sulphate concentration and the stripping solution were studied and based on resulting information, authors proposed a reaction mechanism. Finally, tests were performed using supported liquid membranes (SLM). The results with the synthesized ionic liquids show that [A336/Cy272] was suitable in sulphate, chloride and mixed media, while [C104] is suitable in chloride media. Liquid/liquid extraction tests indicate that it is possible to remove Cu(II) from highly contaminated aqueous solutions (1000 mg/L Cu(II)) using quaternary ammonium type ionic liquids in sulphate, chloride or mixed media, with extraction efficiencies of up to 95%. The best stripping results were obtained in basic and acidic media. In contrast, a fouling problem of the membrane was found in supported liquid membrane tests, which occurs after approximately 4 h of testing. The ionic liquid [A336/Cy272] presented good levels of suitability under different working conditions. The best extractions were obtained at pH higher than 2 and moderate concentrations of total sulphates. Good levels of extraction efficiency were obtained reaching 80% in chloride media. This ultimately led to a hybrid process in which different amounts of sodium chloride were added to solutions that originally contained only sulphates and had low extraction efficiency. On the other hand, IL [C104] was suitable only in chloride media, which performed well in removing Cu (II) from aqueous solutions. The best stripping conditions were obtained in ammoniacal media with an efficiency of 100% and a guarantee of the chemical stability of the ionic liquid used. This is very important because it makes it possible to directly recycling the reagent in a new cycle. Similar efficiency levels are achieved in acidic media, although the latter has the disadvantage of protonating the ionic liquid, which must then be deprotonated to ionic liquid with sodium bicarbonate for later reuse. Stripping in a neutral medium shows a considerable less efficiency than stripping in acidic and basic media. The liquid/liquid extraction demonstrated that authors could achieve good levels of extraction of Cu (II) with ionic liquids based on quaternary ammonium salt. Tests using supported liquid membranes showed that while it is possible to extract the metal, Cu (II) transport is slow. However, this could be improved by scaling up the system and increasing the area of the membrane.

In order to reduce the solvent requirement, emulsion liquid membrane technique was proposed for the benzimidazole separation from aqueous solutions using tri-*n*-octyl methyl ammonium chloride [TOMAC] ionic liquid carrier. The distribution coefficient of benzimidazole between aqueous solution and ionic liquid in membrane phase was studied to optimize the external phase pH [114]. The organic phase consisted of kerosene and *n*-heptane as diluent. At optimized conditions, the emulsion was stable up to 140 min, the breakage of internal phase was <0.5% and 97.5% of benzimidazole was extracted within 12 min with a concentration factor of 5. It was found that benzimidazole concentration in external phase increased due to membrane breakage after 12 min. Authors need to pay more attention to investigate how breakage of internal phase can be minimized with highest extraction of benzimidazole. In another study, polymeric hollow fiber supported ionic liquid membranes were fabricated utilizing Matrimids and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([hmim][Tf₂N]) as the selected polymeric and ionic liquid materials, respectively [115]. The fibers were spun via a dry-wet non solvent-induced phase separation procedure, employing as single layer spinneret extrusion system. Four different types of membranes were fabricated using four morphologically different hollow fiber supports. These membranes take advantage of the fiber morphology combined with a supported ionic liquid to enable more efficient mass transfer than flat membranes. Initially the membranes had a low separation performance for CO₂/H₂; however, upon changing the porosity and support morphology, better permeance and selectivity were achieved. Transport properties of CO₂ and H₂ are reported for hollow fiber membranes containing anionic liquid in the temperature range from 37 to 150°C. The glass transition temperature, Young's modulus, and tensile strength are also reported by authors. The volume fractions of polymer, macro-voids, and micro-voids were determined using a combination of density measurements and an SEM image analysis technique. These quantities were then used to calculate both the bulk fiber porosity and the porosity of the micro-porous region. The surface porosity was also estimated by image analysis. It was observed that the transport and mechanical properties of the fiber were influenced by porosity. In extension and modification of this work, Wickramanayake et al. [48] have fabricated hollow fiber SILMs using both Matrimids and Torlons fiber supports. X-ray CT scan images were successfully used to show the location of IL [1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([C₆mim] [Tf₂N])] within the pore structure of the fibers. It was found that after the fibers were saturated with IL and then underwent a cleaning procedure, that the IL only occupied the micro-porous region of the fiber and the macro-pores that were closed to the fiber core [Fig.19]. When comparing fibers that have a similar porosity, the CO₂ permeance and CO₂/H₂ selectivity are roughly the same regardless of the type of polymer that is used for the support. This resulted from the relatively small co-permeance contribution of the polymer compared with the IL. Furthermore, molecular simulations indicated that Torlons's increased strength was associated with an interlocking of polymer chains that does not occur in the Matrimids. This mechanism has the added benefit that it may prevent IL ions from interspersing within polymer chains, which would disrupt inter chain molecular bonding and decrease mechanical strength. In similar approach, a range of polybenzimidazole (PBI)-[C₄mim][NTf₂] and PI-[C₄mim][NTf₂] composite membranes have been successfully fabricated by Liang et al. [116]. CO₂, CO and H₂ permeability of the PBI membranes with up to 20 wt. % [C₄mim][NTf₂] were measured under 2–6 bar pressure gradients at 100–200°C. The results showed that PBI membranes had high H₂ selectivity to other gases, and [C₄mim][NTf₂] improved gas permeability especially CO₂. CO₂, CO, H₂, N₂ and CH₄ permeability of the PI

membranes with up to 40 wt% [C₄mim][NTf₂] were measured under 2–6 bar pressure gradients at 35–200°C. The results showed that PI membranes had higher gas permeability than the PBI membranes, and they had high CO₂ selectivity to neutral gases such as CO, N₂ and CH₄. The ionic liquid [C₄mim][NTf₂] dispersed in the PI membranes improved the CO₂ permeability without decreasing the selectivity. Overall, the PBI-[C₄mim][NTf₂] and PI-[C₄mim][NTf₂] membranes displayed significant potential for specified gas separation applications, with PI-[C₄mim][NTf₂] particularly suited to CO₂ separation. Hollow fiber supported ionic liquid membranes (SILMs) were tested using the bubble point method to investigate potential failure modes, including the maximum transmembrane pressure before loss of the ionic liquid from the support [117]. Porous hollow fiber supports were fabricated with different pore morphologies using Matrimid® and Torlon® as the polymeric material and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₆mim][Tf₂N]) as the ionic liquid (IL) component. Hollow fiber SILMs were tested for their maximum pressure before failure, with pressure applied either from the bore side or shell side. It was found that the membranes exhibited one or more of three different modes of failure when pressurized: liquid loss (occurring at the bubble point), rupture, and collapse.

In another study, the facilitated separation of CO₂ and SO₂ in a series of supported ionic liquid membranes (SILMs) impregnated with carboxylate-based ILs triethylbutylammonium malonate ([N2224]2[malonate]) and triethylbutylammoniummaleate ([N2224]2[maleate]) (including mono carboxylates and dicarboxylates) was investigated systematically under humidified condition [118]. The effects of transmembrane pressure difference and temperature on the permeability of acidic gases and permselectivity of gas pairs were studied. The permeability of CO₂ in triethylbutylammonium malonate ([N2224]2[malonate]) and triethylbutylammoniummaleate ([N2224]2[maleate]) under the partial pressure of 0.1 bar range from 2147 to 2840 barrers and the permselectivities of CO₂/N₂ and CO₂/CH₄ for them approach to 178–265 and 98–221, respectively. Triethylbutyl ammoniumdimalonate ([N2224][dimalonate]) could facilitate the permeation of SO₂ with a permeability of 7208 barrers under the transmembrane pressure difference of 0.05 bar, and the permselectivities of SO₂/N₂, SO₂/CH₄ and SO₂/CO₂ are 585,271 and 18 respectively. The mechanism of facilitated separation was explained by authors from the reversible reactions of CO₂ and SO₂ with different forms of dicarboxylate-based ILs. Authors have also compared the performance of [N2224][dimalonate] for the separation of SO₂ with a normal IL ([emim][CF₃SO₃]) and its mixture with glucose pentaacetate (GPA) [119], as shown in **Table 4**. It can be seen that [N2224][dimalonate] has lower permeability of SO₂ in comparison with [emim][CF₃SO₃] and [emim][CF₃SO₃]+GPA mixture. The reason as suggested by authors was that although [N2224][dimalonate] could reversibly react with SO₂ and act as a carrier for the transport of SO₂, its viscosity (170 mPas) was larger than [emim][CF₃SO₃] and [emim][CF₃SO₃]+GPA mixture (100 mPas). The two factors counteract with each other on the influence of the permeability of SO₂. However, the permselectivity of SO₂/N₂, SO₂/CH₄, and SO₂/CO₂ in [N2224][dimalonate] was much higher than that in [emim][CF₃SO₃] and [emim][CF₃SO₃]+GPA mixture. Therefore, [N2224][dimalonate] could be regarded as an efficient medium by authors for the selective separation of SO₂ from other gases.

In recent study, Ferreira et al. [120] have examined the possibility for the use of ionic liquids as alternative solvents for the removal of thiols at room-temperature from n-dodecane used as jet fuel model stream. This works have evaluated

the use of supported ionic liquid membranes (SILMs) for the selective removal of thiols applying vacuum in the downstream side. This approach consists in the incorporation of the ionic liquid inside the membrane pores, while due to the vacuum applied, the thiol compound was scrubbed. To study the target solute transport from the feed to the ionic liquid, extraction experiments were carried out using different 1-ethyl-3-methylimidazolium cation-based ionic liquids. The mass transfer resistance was found to be higher in the ionic liquid phase, which resulted mainly from the high ionic liquid viscosities, hindering the thiol transport. The results obtained by authors showed that the ionic liquids were properly incorporated inside the pores of the membrane support. The systems tested presented low mass transfer coefficients, $0.67 \times 10^{-7} \text{ m s}^{-1}$, $1.72 \times 10^{-7} \text{ m s}^{-1}$ and $2.01 \times 10^{-7} \text{ m s}^{-1}$ for the systems with $[\text{C}_2\text{mim}][\text{MeSO}_4]$, $[\text{C}_2\text{mim}][\text{CF}_3\text{SO}_3]$ and $[\text{C}_2\text{mim}][\text{NTf}_2]$, respectively, controlled by the thiol transport in the ionic liquid phase. This behavior can be overcome due to the permanent removal of the ionic liquid in the SILM to the receiving phase. From the positive pressure difference experiments, **Fig. 20** showed that the SILMs prepared with hydrophobic PVDF support are more stable than the ones prepared with hydrophilic PVDF. Among the ionic liquids tested, it was concluded that the $[\text{C}_2\text{mim}][\text{CF}_3\text{SO}_3]/\text{hb-PVDF}$ SILM is the most stable membrane, presenting losses lower than 2% up to 1.4 bar, followed by the $[\text{C}_2\text{mim}][\text{NTf}_2]$ up to 1 bar. This work proposed the possibility for an integrated extraction/stripping of thiols from “jet-fuel” streams by using two membrane contactors in series, where extraction to a selected ionic liquid takes place in the first contactor, and stripping from the ionic liquid occurs in a second contactor. Using this configuration, the ionic liquids used can be continuously regenerated and recycled between both contactors.

3.6 Polymer inclusion membrane (PIM)

Of late, polymer inclusion membrane have gained paramount importance in the field of separation science as indicated by published papers in last five years [**1, 31, 56, 121-123**]. Facilitated transport of Cr(VI) ions from aqueous chromate donor phase ($2 \times 10^{-4} \text{ k mol/m}^3$) through polymer inclusion membranes (PIMs) using a newly synthesized 5,17-di-tert-butyl-11-piperidinomethyl-25,26,27,28-tetrahydroxycalix[4]-arene (carrier), as ion carrier, has been investigated by Kaya et al. [**124**]. The Cr(VI) passed through a PIM comprised of cellulose triacetate (CTA) as a support and 2-NPOE as a plasticizer. The prepared PIM was characterized with Fourier transform infrared (FT-IR) spectroscopy and the atomic force microscopy (AFM) techniques as well as with contact angle measurements. The efficiency of Cr (VI) transport through the PIM was investigated by studying the effects of carrier concentration on the donor phase as well as by measuring the amount of plasticizer in the membrane, the pH in the acceptor phase, the effect of acid type in donor phase, and the membrane's stability and thickness. The kinetic parameters were calculated as permeability coefficient (P), flux (J), and diffusion coefficient (D). The transport permeability, fluxes, and diffusion coefficient of carrier were observed to increase from 1.0 to 1.75 mL (2-NPOE/ 1 g CTA) until the limited value was reached. At that point, the transport permeability, fluxes, and diffusion coefficient of carrier decreased. Increasing the amount of 2-NPOE, which has a high dielectric constant, increases the membrane thickness and viscosity, so it began to decrease after the maximum value. Experiments on Cr(VI) transport across the PIM were carried out with five different thicknesses and

varying amounts of CTA. The prepared membranes were 42, 48, 54, 60, and 66 μm thick. The results indicated that the flux values decreased as the membrane thickness increased, which could be explained by Fick's first law as given below:

$$J = D \frac{\Delta C}{\Delta X}$$

Assuming that d is the length of the transport path $\Delta x = d$, one can create eq 8 according to the initial concentration of $\Delta C \approx C_i$ as follows.

$$J_i = D_i \frac{C_i}{d}$$

The inverse relationship between the flux of Cr(VI) and membrane thickness was found to be a straight line, which confirms the existence of a rate-limiting transport due to the diffusion of a metal complex across a membrane. Using the slope of the obtained relation $1/J$ vs d , the authors estimated the apparent diffusion coefficient of the Cr(VI)-containing species in the membrane phase. The transport efficiency of Cr (VI) was observed to be 99.38% after 6 h under optimized conditions. Although authors claimed that developed PIMs could be used in the long term for the removal of Cr (VI) from industrial waste waters but more experiments are required to establish its feasibility on pilot scale.

In another study PIM was investigated by Kolev et al. [125] for the extraction and separation of uranium (UO_2^{2+}) from acidic sulfate solutions. Homogeneous, transparent and mechanically stable PIMs with PVC as the base-polymer and Aliquat336, Cyanex272, TBP or D2EHPA as the extractant were obtained and tested for their ability to extract U(VI) from its acidic sulfate solutions. The membrane with composition 40% (m/m) D2EHPA and 60% (m/m) PVC was found to be superior in its ability to extract U(VI) in comparison with the other PIM studied. Quantitative back-extraction was achieved with $4\text{M H}_2\text{SO}_4$. Preliminary transport experiments involving $4\text{M H}_2\text{SO}_4$ as the stripping reagent demonstrated the potential of this membrane for the separation of U (VI) from its acidic sulfate solutions with possible applications in the clean-up of contaminated effluents from the uranium mining and nuclear industries. A new method for the determination of the stoichiometry of membrane-extracted complexes was proposed and applied to the U (VI)-PIM extraction system studied. The composition of the U (VI)-D2EHPA complex was determined as $\text{UO}_2 \cdot \text{A}_2 \cdot (\text{HA})_2$ where HA and A^- are D2EHPA and its conjugated base, respectively. The applicability of the proposed method to solvent extraction systems was also demonstrated [with uranium fluxes as high as $4.85 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$].

The effect of the base-polymer and carrier concentration on the physical-chemical characteristics of polymer inclusion membranes (PIMs) was investigated by Vazquez et al. [126]. Two typical polymers used to fabricate PIMs have been tested i.e. poly vinyl chloride (PVC) and cellulose triacetate (CTA), and different amounts of the ionic liquid (IL) Aliquat-336, used as extractant, were the PIMs constituents. The resulting PIMs have been characterized using different techniques to provide information on both the surface and bulk material properties. XPS results did not practically show differences in the surfaces of CTA and PVC based membranes with similar Aliquat336 content, and the total surface coverage for Aliquat-336 concentration higher than 40% (w/w) was obtained, which was also corroborated with the

results of contact angle measurements. However, membrane elastic response seems to be strongly dependent on both base- polymer and Aliquat-336 concentration, which affected Young modulus and elongation at break. The IL concentration also increased dielectric constant and the conductivity of the PIMs from both polymers according to impedance spectroscopy results, providing a rather conductive character to both kind of samples for Aliquat-336 content higher than 40% (w/w) (average conductivity around 10^{-3} ($\Omega \text{ m}^{-1}$)). CTA and PVC-based PIMs with Aliquat-336 content around 45% have been used in order to compare the influence of the polymer on the transport of As (V). The analysis of PIMs manufactured from different base polymers and varying the IL Aliquat 336 content has been performed by different techniques. XPS analysis of PIMs using PVC as base polymer and the IL Aliquat 336 as extractant showed almost total membrane surface coverage for Aliquat-336 content higher than 40%, when chlorine concentration associated to the polymer support was practically undetectable; moreover, the similarity of nitrogen and chlorine atomic concentration percentages associated to Aliquat-336 also extends this result to the CTA-based PIMs, which was also supported for contact angle results. The effects of both base polymer and extractant concentration in the bulk membrane have been analyzed by IR, elastic and impedance spectroscopy measurements. According to IR spectra, the incorporation of Aliquat336 did not seem to cause any significant chemical change in the studied PIMs. However, the differences obtained in the stress–strain curves depending on the base polymer clearly showed the softer and tougher character of the PVC-based membranes, and the increase of Aliquat336 significantly enlarged the elastic behavior of both kinds of samples. Impedance spectroscopy results also showed the effect to Aliquat 336 content on characteristic material parameters as conductivity and dielectric constant, but their values hardly depended on the CTA or PVC base-polymer. Characterization results indicated that Aliquat336 concentration higher than 40% seems to be necessary for membrane surface coverage, when the polymers' specific characteristics are lost. This point was confirmed by ion (As(V) species) transport measurements performed with CTA~48% Aliquat336 and PVC~ 45% Aliquat336 membranes, which also showed the potential of the studied PIMs for application in water remediation with this kind of contaminant.

In another work, a development of polymeric inclusion membranes for the cations separation was reported. The membrane was made up of cellulose triacetate (CTA) with a tributyl phosphate (TBP) incorporated into the polymer as metal ions carrier [127]. The transport of lead (II) and cadmium (II) ions in two membrane systems, PIM coupled with photo-chemical electrode using TBP as carrier and 2-nitro phenyl octyl ether (NPOE) or tris ethylhexyl phosphate (TEHP) as plasticizer was investigated. The membranes: polymer + plasticizer + carrier were synthesized and characterized by FTIR, X-ray diffraction and scanning electron microscopy (SEM). Transports of lead and cadmium have been studied using these systems and the results were compared to commercial cation exchange membrane (CRA). The obtained results showed that for Pb^{2+} ion, the concentrations of the strip phase increased using synthesized membranes. The conduction band of the delafossite CuFeO_2 (-1.25V SCE) yields a thermodynamically M^{2+} ($=\text{Pb}^{2+}$, Cd^{2+}) photo electrodeposition and speeds up the diffusion process. The oxide crystallizes in the delafossite structure and absorbs over the whole solar spectrum in addition to being low cost and exhibits long-term chemical stability. The high energetic position of its conduction band is appropriately positioned to allow an efficient charge separation of the electron/hole pairs leading to metal deposition. The cations flow was considerably speeded up through the membrane with

illuminated CuFeO_2 electrode followed by the electrodeposition on Pt electrode. In all the cases, the potential of the electrode M/M^{2+} in the feed compartment increased until a maximum value, reached at 100 min above which it undergoes a diminution.

Regulatory controls to limit mercury emissions in waters have impacted on the development of membrane extraction-based methodologies for its separation. The specific advantages (effective carrier immobilization, easy preparation, versatility, and good mechanical properties) of PIMs make them suitable for this purpose. In this work a novel procedure using PIMs for mercury separation with a commercial available extractant (Cyanex 471X) was described and evaluated through the determination of the efficiency parameters (permeability, selectivity, stability) and membrane characterization [128]. Using a membrane composed of 30% cellulose triacetate (CTA), 60% 2-nitrophenyl octyl ether (NPOE), and 10% w/w Cyanex 471X and 0.1 mmol dm^{-3} Hg(II) solution prepared in 0.01 mol dm^{-3} HCl was transported to a 0.05 mol dm^{-3} NaCl solution at pH 12.3 with permeability values in the feed and strip phases of 0.25 and 0.15 cm min^{-1} , respectively. A diffusive Fickian-type mechanism was inferred from the results. High separation factors ranging between 2 and 5900, less than 11% of competing metal ions transported, active transport of the metal ion and a successful reuse of the PIM were achieved. Optimized PIMs using Cyanex 471X represent an interesting alternative for Hg (II) removal from waters showing high efficiency factors and easy implementation. In the area of fission product separations, transport behavior of ^{137}Cs from nitric acid feed was investigated using cellulose triacetate plasticized polymer inclusion membrane (PIM) containing several crown ether carriers viz. di-benzo-18-crown-6 (DB18C6), di-benzo-21-crown-7 (DB21C7) and di-*tert*-butylbenzo-18-crown-6 (DTBB18C6) [129]. The PIM was prepared from cellulose triacetate (CTA) with various crown ethers and plasticizers. DTBB18C6 and tri-*n*butyl phosphate (TBP) were found to give higher transport rate for ^{137}Cs as compared to other carriers and plasticizers. Effect of crown ether concentration, nitric acid concentration, plasticizer and CTA concentration on the transport rate of Cs was also studied. The Cs selectivity with respect to various fission products obtained from an irradiated natural uranium target was found to be heavily dependent on the nature of the plasticizer. This work showed that by choosing a proper plasticizer, one can get either good transport efficiency or selectivity. Though TBP plasticized membranes showed good transport efficiency, it displayed poor selectivity. On the other hand, an entirely opposite separation behavior was observed with 2-nitrophenyloctylether (NPOE) plasticized membranes suggesting the possible application of the later membranes for the removal of bulk ^{137}Cs from the nuclear waste. The stability of the membrane was tested by carrying out transport runs for nearly 25 days. The present studies have indicated that though quantitative ^{137}Cs estimation is possible using the TBP plasticized membrane; selective pre-concentration of ^{137}Cs from a host of fission products is feasible using the NPOE plasticized membrane. This can certainly help the analysis of the ^{137}Cs activity in complex acidic radioactive wastes, such as the high level waste.

Separation of zinc (II) and copper (II) ions from aqueous solutions by synergistic extraction and transport through polymer inclusion membranes (PIMs) has been investigated by Pospiech [130]. Zn(II) ions were successfully separated from Cu(II) ions in solvent extraction process using 0.025 M TOPO and 0.06 M Aliquat 336 in kerosene. PIMs containing a mixture of TOPO and Aliquat 336 as the ion carrier have been prepared and the facilitated transport of Zn(II) and Cu(II)

ions has been studied. Studies of transport of Zn (II) and Cu(II) from chloride media through cellulose triacetate membranes containing the mixture of TOPO and Aliquat 336 as ion carrier showed that the initial flux of Zn(II) ions was dependent on membrane composition, *i.e.*, concentration of polymer support, ion carrier as well as concentration of the plasticizer. Finally, the separation system presented by authors was demonstrated to be useful for the separation of Zn (II) and Cu (II) from aqueous chloride solutions.

In another work of Pospiech [131], selective transport of cobalt (II) and lithium (I) ions from aqueous chloride solutions through polymer inclusion membranes (PIMs) was investigated. Triisooctylamine (TIOA) has been applied as the ion carrier in membrane and effects of several parameters on the transport of Co (II) and Li (I) were studied. The results showed that Co(II) ions were effectively removed from source phase through PIM containing 32 wt.% TIOA, 22 wt.% CTA (cellulose triacetate) and 46 wt.% ONPOE (*o*-nitrophenyl octyl ether) or ONPPE (*o*-nitrophenyl pentyl ether) into deionized water as the receiving phase. The results indicated that there is a possibility of PIMs application to recover Co (II) and Li (I) from aqueous chloride solutions. Polymer inclusion membranes with triisooctylamine as ion carrier provide an attractive alternative to conventional solvent extraction methods for the separation of cobalt (II) and lithium (I). The results showed that cobalt (II) ions can be effectively recovered from aqueous chloride solutions containing lithium (I) in transport process across PIMs. The transport using triisooctylamine as the ion carrier showed high selectivity Co (II) > Li (I). The transport process is affected by the initial concentration of metal ions and hydrochloric acid concentration in the source phase, as well as membrane composition, *i.e.* ion carrier concentration and the type of plasticizer. The results showed that the % recovery of Co(II) and Li(I) using PIM with triisooctylamine, after 24 h reached 74.5% and 5.3%, respectively. The highest selectivity coefficient in this process was 4.1. Finally, authors claimed that this study was useful for the separation of Co (II) and Li (I) from aqueous chloride solutions.

In another study, influence of carrier concentration in membrane on citric acid transport rate through PIM was examined by Gajewski et al. [132]. Observed dependence is not linear with evident percolation threshold. Also, a small increase of the transport rate with increasing alkyl chain length from 10 to 14 was observed (for the same mass fraction of carrier in membrane). On the basis of the obtained results, the transport mechanism of citric acid through PIM was proposed. In accordance with suggestions of other authors, the presence of the percolation threshold and the absence of flux decreasing with carrier's molecule increasing proved that citric acid is transported in accordance with fixed-site jumping mechanism (Fig. 21). However, as could be seen (Fig. 22) the influence of feed phase concentration on the $J \cdot d$ value is mostly linear which was not completely confirmed the proposed mechanism. But comparing the results obtained in this work with results obtained by other authors for the transport of citric acid through ion exchange membrane [133], a very similar curve shape could be observed. The authors calculated that citric acid in this case was transported mainly by the carrier type mechanism but some part of them is transported by simple diffusion.

PIMs containing TODGA (N,N,N'-tetra-*n*-octyl diglycolamide) were evaluated by Mahanty et al.[134] for the separation of actinide ions such as Am³⁺, Pu⁴⁺, UO₂²⁺ and Th⁴⁺ from acidic feeds. The uptake studies were carried out using feed solutions containing varying concentrations of nitric acid and showed the trend: Am³⁺ > Pu⁴⁺ > Th⁴⁺ > UO₂²⁺. The

actinide ion transport efficiencies with TODGA containing PIMs followed the same trend as seen in the uptake studies. The AFM patterns of the PIMs changed when loaded with Eu^{3+} carrier (used as a surrogate for Am^{3+}) while the regenerated membranes have displayed comparable morphologies. Diffusion coefficient values were experimentally obtained from the transport studies and were found to be $8.89 \times 10^{-8} \text{cm}^2/\text{s}$ for Am^{3+} transport.

In another study, the uptake studies with TODGA based PIMs with the optimized composition indicated reasonably high uptake efficiency for the actinide ions [135]. Poor uptake efficiency for uranyl ion could be attributed to its poor extraction with the diglycolamide extractants. The role of plasticizer concentration and CTA concentration was not very important and the transport rates depended primarily on the carrier concentration. As the uptake values can be directly correlated to the extraction efficiency of the diglycolamide, the lower uptake of Pu (IV) as compared to that of Am (III) conform to the reverse micellar mechanism prevalent in case of TODGA. The transport studies have conformed to similar trend as displayed in the SLM based separation systems. However, the diffusion rates are found to be rather low and longer transport time is needed for attaining >90% transport of the metal ions (Am (III), Th (IV) and Pu (IV)), while U (VI) transport was poor.

PIM has also been intensively studied for developing cost-effective and environmentally benign separation processes for succinic acid by Pratiwi et al. [136]. PIMs are formed by casting a solution containing a carrier (Aliquat 336), plasticizer, and base polymer (poly(vinyl chloride)) to form a thin, flexible, and stable film. It was observed that succinate successfully permeated the PIM containing Aliquat 336 and uphill transport using a feed solution with pH 4 and Na_2CO_3 solution as the stripping phase was reported. PIMs show complex permeation behavior involving un-dissociated, mono-anionic, and di-anionic forms of succinic acid as the species permeated. The mono-anionic form of succinic acid showed the largest permeability among the three forms, with the optimum pH range for succinic acid permeation being approximately 4–5.

A novel approach based on the use of nanometallic-decorated hollow fibers to assist electromembrane extraction was proposed by Payan et al. [137]. Micro porous polypropylene hollow fibers, on which nanometallic silver was deposited, was used for the first time as liquid membrane support in electromembrane extraction (EME). Different methods for the generation/deposition of silver nanoparticles (AgNPs) were studied. The best results were obtained with chemical reduction of silver nitrate using NaBH_4 in aqueous solution followed by direct deposition on the hollow fibers. The extraction performance of the new supports was compared with a previously developed EME procedure used for the extraction of selected non-steroidal anti-inflammatory drugs (NSAIDs), resulting in an increase in the extraction ratio by a factor of 1.2–2 with a 30% reduction in the extraction time. The new nanometallic-decorated supports open new possibilities for EME due to the singular properties of nanometallic particles, including chemical fiber functionalization. More work is required by authors to fully understand the processes involved focusing on fundamentals, instrumentation, and applications. Nanometallic-decorated supports may become a promising future in sample preparation, especially in miniaturized analytical systems.

4. MATHEMATICAL MODELING ASPECTS OF SIMALE TECHNIQUES

In order to scale up SIMALE membrane processes, mathematical modeling is important component which can predict the transport behavior of solute with respect to mass transfer modeling and rate controlling steps. The important aspects of mathematical modelling is already published by Bringas et al. [8, 88,148], hence mathematical modeling is not covered in detail in this review paper. The different approaches adopted for mathematical modeling for various SIMALE techniques are summarized in **Table 5 [138-152]**.

5. CONCLUDING REMARKS AND FUTURE DIRECTIONS

SIMALE techniques offer the advantages of both solvent extraction and membrane separations. These techniques have established an increasing number of applications related to the recovery of valuable compounds from wastewaters and industrial effluents due to its potential to replace conventional processes by accomplishing selective and efficient transport of specific components and providing reliable options for a sustainable growth. In particular, liquid-membrane separation promote the uphill and selective transport of the target species by the coupling between mass transfer and chemical reaction. However, the stand-alone application of individual membrane processes often fails to recover all the possible valuable materials present in complex aqueous streams. Therefore, the development of integrated processes consisting of single membrane separation stages is a promising strategy to design eco-innovative processes. In order to fulfill this criteria, emphasis has been shifted to hollow-fiber contactors as well as hollow-fiber NDSX technique that can have surface-to-volume ratio as high as $10,000 \text{ m}^2/\text{m}^3$. Hollow-fiber contactors have been used in three different modes: namely, HFNDSX extraction, PEHFSD and HFSLM, for extraction/removal of organic compounds, metal extraction/separation and in radioactive waste processing. In these process, intelligent membrane engineering can help to realize the process intensification strategy being followed for SIMALE techniques.

In order to overcome the stability problems encountered in conventional LM systems, HFRLM was recently proposed. This technique is based on the surface renewal theory and integrates the advantages of the HFM extraction process, the liquid film permeation process, and other LM systems. Ionic liquids (ILs) are another new solution being investigated by several researchers with a view to ensuring the stabilized and consistent performance of LMs. Similarly, super critical fluid based membrane extraction have gained paramount importance in last few years and several studies are reported worldwide by researchers.

Many well-known producers of membrane and membrane modules today offer commercial membrane contactors as part of their product portfolio. Hollow fiber membrane contactors are used for degassing liquids around the world. They are widely used for O_2 removal from water as well as CO_2 removal from water. They have displaced the vacuum tower, forced draft deaerator, and oxygen scavengers for over last few years.

The steady increase in research on PIMs has established a wide range of laboratory- and industry-based separation applications. Their attraction for use in industry is based on the fact that PIMs can be formulated using most of the commercially available SX reagents and they do not require a large inventory of diluents. In addition, losses of PIM

components to the corresponding aqueous phases are small compared to those in SX systems, and PIMs have the advantage of allowing extraction and back-extraction to be conducted in a single step. Most research on PIMs has been focused on flat-sheet membranes; however, industrial applications will require very high surface area to solution volume ratios, and so other membrane configurations such as HF or spiral wound modules will be required to achieve this aim. PIMs containing macro cyclic units with the ability to entrap specific metal ion are getting special attention for fission products separations. These are cellulose triacetate (CTA)-based membranes with inclusion carriers that have specificity toward radionuclides. The membrane type, PIM or polymeric plasticizer membrane (PPM), is claimed to combine the virtue of rapid transport with high selectivity and ease of setup and operation, exhibiting at the same time excellent durability. Because this type of membrane is independent of organic solvents due to the fact that the carrier molecules are trapped within the CTA matrix, they do not suffer from loss of organic solvents nor as much leaching of carrier into the aqueous phases. The PIM entraps the macro cyclic carriers in the membrane matrix during the casting process, effectively inhibiting carrier loss to adjacent aqueous phases.

Due to several merits, SIMALE technique (SLMs) were studied in the nuclear industry for radioactive waste treatment and removal of actinides and fission products from the waste after reprocessing of nuclear fuel. Radionuclides, such as cesium, strontium, cerium, and europium, were separated from radioactive solutions to reduce the radiotoxicity of the waste. Uranium, plutonium, and americium removal from the wastes produced in the back end of fuel cycle, as well as the effective methods for actinide partitioning is described in this review.

HFM technology has found pilot-plant and full-scale applications in the fields of chemical and pharmaceutical technology, biotechnology, food processing and environmental engineering. They are functioning well with consistent performance.

6. ACKNOWLEDGEMENTS

Authors thank to Shri. Amitava Roy, Chief Executive, Nuclear Recycle Board, Shri. K K Singh, Project Director, INRPC, Nuclear Recycle Board, Tarapur and Shri. Sanjay Pradhan, Chief Superintendent, TNRPO, Shri. K Dubey, Plant Superintendent, TRP and Dr. C.B. Patil, Superintendent, PC & PR, TRP, Nuclear Recycle Board, Tarapur for supporting this paper.

1. REFERENCES

- [1]. Anil K Pabby, A. M. Sastre, State-of-the-art review on hollow fiber contactor technology and membrane-based extraction processes, *Journal of Membrane Science*, 430 (2013) 263–303.
- [2] A.K. Pabby, S.S.H. Rizvi, A.M. Sastre, *Hand Book of Membrane Separations: Chemical, Pharmaceutical, Food and Biotechnological Application*, New York, USA, CRC Press, 1st Edition, 2008, 2nd edition, 2015.
- [3] Kamalesh K. Sirkar, , Anthony G. Fane, Rong Wang, S. Ranil Wickramasinghe, Process intensification with selected membrane processes, *Chemical Engineering and Processing*, 87 (2015) 16–25.
- [4] E. Drioli, A.I. Stankiewicz, F. Macedonio, Membrane engineering in process intensification—An overview, *Journal of Membrane Science*, 380 (2011) 1–8.
- [5] E. Drioli, E. Curcio, G. Di Profio, State of the art and recent progresses in membrane contactors, *Transactions of IChemE, Part A: Chemical Engineering Research and Design*, 83 (A3) {2005} 223–233.
- [6] P. Bernardo, G. Clarizia, Potential of membrane operations in redesigning industrial processes. The ethylene oxide manufacture, *Chemical Engineering Transactions*, 25 (2011) 617–622.
- [7] H.J. Bart, C. Drumm, M.M. Attarakih, Process intensification with reactive extraction columns, *Chemical Engineering and Processing*, 47 (2008) 745–754.
- [8] E. Bringas, M.F. San Román, J.A. Irabien, I. Ortiz, An overview of the mathematical modeling of liquid membrane separation processes in hollow fiber contactors, *Journal of Chemical Technology and Biotechnology*, 84 (2009) 1583–1614.
- [9] H. Escalante, A.I. Alonso, I. Ortiz, A. Irabien, Separation of l-phenylalanine by non-dispersive extraction and back extraction. Equilibrium and kinetic parameters, *Sep. Sci. Technol.*, 33 (1998) 119.
- [10] A.M. Urriaga, M.I. Ortiz, E. Salazar, J.A. Irabien, Supported liquid membranes for the separation-concentration of phenol. 2. Mass-transfer evaluation according to fundamental equations, *Industrial and Engineering Chemistry Research*, 31 (1992) 1745–1753.
- [11] F.X. Pierre, I. Souchon, V. Athes-Dutour, M. Marin, Membrane-based solvent extraction of sulfur aroma compounds: influence of operating conditions on mass transfer coefficients in a hollow fiber contactor, *Desalination*, 148 (2002) 199.
- [12] Basudev Swain, Chinmayee Mishra Jinki Jeong, Jae-chun Lee, Hyun Seon Hong, B.D. Pandey, Separation of Co(II) and Li(I) with Cyanex 272 using hollow fiber supported liquid membrane: A comparison with flat sheet supported liquid membrane and dispersive solvent extraction process, *Chemical Engineering Journal*, 271 (2015) 61–70.

- [13] Lihle D. Mafu & Titus A. M. Msagati, The simultaneous stripping of arsenic and selenium from waste waters using hollow-fibre supported liquid membranes, *Environ Monit Assess*, 186 (2014)8865–8874.
- [14] B. Galán, F. San Román, A. Irabien, I. Ortiz, Viability of the separation of Cd From highly concentrated Ni–Cd mixtures by non-dispersive solvent extraction, *Chem. Eng. J.*, 70 (1998) 237.
- [15] A. K. Dinkar, Suman Kumar Singh, S. C. Tripathi, R. Verma, and A. V. R. Reddy, Carrier Mediated Transport of Thorium from Nitric Acid Medium using 2-Ethyl Hexyl Hydrogen 2-Ethyl Hexyl Phosphonate (PC88A)/N-Dodecane as Carrier, *Separation Science and Technology*, 48 (2013)728–735.
- [16] J. Laso, V. García, E. Bringas, A. M. Urtiaga, and I. Ortiz, selective recovery of zinc over iron from spent pickling wastes by different membrane-based solvent extraction process configurations, *Ind. Eng. Chem. Res.* 54 (2015) 3218–3224.
- [17] Malgorzata Ulewicz and Elzbieta Radzaminska-Lenarcik, Application of Polymer and Supported Membranes with 1-Decyl-4-Methylimidazole for Pertraction of Transition Metal Ions, *Separation Science and Technology*, 49 (2014) 1713–1721.
- [18] Pradeep C. Rout and Kadambini Sarangi, Comparison of hollow fiber membrane and solvent extraction techniques for extraction of cerium and preparation of ceria by stripping precipitation, *J Chem Technol Biotechnol.*, 90 (2015) 1270–1280.
- [19] B. Raghuraman, J. Wiencek, Extraction with emulsion liquid membranes in a hollow-fiber contactor, *AIChE J.*, 39(1993) 1885.
- [20] A.J.Walsh, H.G. Monbouquette, Extraction of Cd²⁺ and Pb²⁺ from diluted aqueous solution using metal-sorbing vesicles in a hollow-fiber cartridge, *J. Membr. Sci.*, 84 (1993), 107.
- [21] R. Klaassen, A.E. Jansen, B.A. Bult, F.I.H.M. Oesterholt, J. Schneider, Removal of hydrocarbons from wastewater by pertraction, in: *Proceedings of the 7th International Symposium on Synthetic Membranes in Science and Industry*, University of Tübingen, Tübingen, Germany, 1994, 316.
- [22] W.S. Ho, T.K. Poddar, New membrane technology for removal and recovery of chromium from wastewaters, *Environ. Prog.*, 20 (2001) 44.
- [23] K. Klaassen, A.E. Jansen, Selective recovery of heavy metals with emulsion pertraction, in: *Proceedings of the Euromembrane 2004 Hamburg (Germany)*, 2004, p. 428.

- [24] D. He, S. Gu, M. Ma, Simultaneous removal and recovery of cadmium(II) and CN⁻ from simulated electroplating rinse wastewater by a strip dispersion hybrid liquid membrane (SDHLM) containing double carrier, *J. Membr. Sci.*, 305 (2007) 36.
- [25] D. de Agreda, I. Garcia-Diaz, F.A. López and F.J. Alguacil, Supported liquid membranes technologies in metals removal from liquid effluents, *Revista De Metalurgia*, 47 (2011)146-168.
- [26] J.V. Sonawane, A.K. Pabby, A.M. Sastre, Au(I) extraction by LIX-79/*n*-heptane using the pseudo-emulsion-based hollow-fiber strip dispersion (PEHFSD) technique, *J. Membr. Sci.*, 300 (2007)147.
- [27] C. W. Zhang, Z. Cui, Y. Ren, H. Dai, J. Meng, Simultaneous removal and recovery of copper(II) from acidic wastewater by hollow fiber renewal liquid membrane with LIX984N as carrier, *Chem. Eng. J.*, 157 (2010) 230–237.
- [28] Z.Q. Ren, W.D. Zhang, Y.M. Liu, Y. Dai, C.H. Cui, New liquid membrane technology for simultaneous extraction and stripping of copper(II) from wastewater, *Chem. Eng. Sci.*, 62 (2007) 6090–6101.
- [29] Weidong Zhong, Z.Q. Ren, Huilin Zhang, Junteng Meng, Shuguang Liu, Wang, Extraction separation of Cu(II) and Co(II) from sulfuric solutions by hollow fiber renewal liquid membrane, *J. Membr. Sci.*, 365 (2010) 260–268.
- [30] J. Liu, W. Zhang, Z. Ren and J. Ma, The separation and concentration of Cr(VI) from acidic dilute solution using hollow fiber renewal liquid membrane, *Ind. Eng. Chem. Res.*, 48 (2009) 4500–4506.
- [31].L.D. Nghiem, P. Mornane, I.D. Potter, J.M. Perera, R.W. Cattrall, S.D. Kolev, Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs), *Journal of Membrane Science*, 281 (2006) 7–41.
- [32] A.M. St John, R.W. Cattrall, S.D. Kolev, Transport and separation of uranium(VI) by a polymer inclusion membrane based on di-(2-ethylhexyl) phosphoric acid, *Journal of Membrane Science*, 409–410 (2012) 242–250.
- [33] Duo Wang, Jiugang Hu, Dabiao Liu, Qiyuan Chen, Jie Li, Selective transport and simultaneous separation of Cu(II), Zn(II) and Mg(II) using a dual polymer inclusion membrane system, *Journal of Membrane Science* 524 (2017) 205–213.
- [34] A.M. St John, R.W. Cattrall, S.D. Kolev, Extraction of uranium(VI) from sulfate solutions using a polymer inclusion membrane containing di-(2-ethylhexyl) phosphoric acid, *Journal of Membrane Science*, 364 (2010)354–361.
- [35] Aida Garcia-Rodríguez, Víctor Matamoros, Spas D. Kolev, Clàudia Fontàs, Development of a polymer inclusion membrane (PIM) for the preconcentration of antibiotics in environmental water samples, *Journal of Membrane Science*, 492 (2015) 32–39.
- [33] Kahina Annane, Amar Sahmoune, Patrice Montels, Sophie Tingry, Polymer inclusion membrane extraction of cadmium(II) with Aliquat 336 in micro-channel cell, *Chemical Engineering Research And Design*, 94 (2015)605–610.

- [37] M. Matsumoto, Y. Inomoto, K. Kondo, Selective separation of aromatic hydrocarbons through supported liquid membranes based on ionic liquids, *J. Membr. Sci.*, 246 (2005) 77–81.
- [38] M.T. Coll, A. Fortuny, A.M. Sastre, Boron reduction by supported liquid membranes using ALiCY and ALiDEC ionic liquids as carriers, *Chemical Engineering Research and Design*, 92 (2014)758–763.
- [39] P. Scovazzo, A.E. Visser, J.H. Davis Jr., R.D. Rogers, C.A. Koval, D.L. DuBois, R.D. Noble, Supported ionic liquid membranes and facilitated ionic liquid membranes ionic liquids: industrial applications to green chemistry, in: R.D. Rogers, K.R. Seddon (Eds.), *ACS Symposium Series 818*, Am. Chem. Soc., Washington, DC, 2002, 68.
- [40] F.J. Hernandez-Fernandez, A.P. de los Rios, F. Tomas-Alonso, D. Gomez, G. Villora, Kinetic resolution of 1-phenylethanol integrated with separation of substrates and products by a supported ionic liquid membrane, *J. Chem. Technol. Biotechnol.*, 82 (2007) 190–195.
- [41] Mamoun Althuluth, Johan P. Overbeek, Hans J. Van Wees, Lawien F.Zubeir, Wim G.Haije, Abdallah Berrouk, Cor J.Peters, Maaik C.Kroon, Natural gas purification using supported ionic liquid membrane, *Journal of Membrane Science*, 484 (2015)80–86.
- [42] Zhongde Dai a, Richard D.Noble b, DouglasL.Gin b, Xiangping Zhang c, Liyuan Deng, Combination of ionic liquids with membrane technology:Anew approach for CO₂ separation, *Journal of Membrane Science* 497(2016)1–20
- [43] F.J. Alguacil, M. Alonso, F.A. Lopez, A. Lopez-Delgado, Application of pseudoemulsion based hollow fiber strip dispersion (PEHFSD) for recovery of Cr(III) from alkaline solutions, *Sep. Purif. Technol.*, 66(2006) 586–590.
- [44] F.J. Alguacil, M. Alonso, F.A. Lopez, A. Lopez-Delgado, I. Padilla, H. Tayibi, Pseudo-emulsion based hollow fiber with strip dispersion pertraction of iron(III) using (PJMTH⁺)₂ (SO₄²⁻) ionic liquid as carrier, *Chem. Eng. J.*, 157 (2010), 272–366.
- [45] L.C. Branco, J.G. Grespo, C.A.M. Afonso, Studies on the selective transport of organic compounds by using ionic liquids as a novel supported liquid membranes, *Chem. Eur. J.*, 8 (2002)3865–3871.
- [46] P. Bonhote, A.-P. Dias, N. Papageorgio, K. Kalayanasundaram, M. Gratzel, Hydrophobic, highly conductive ambient-temperature molten salts, *Inorg. Chem.*,35(1996) 1168–1178.
- [47] T. Welton, Room-temperature ionic liquids. Solvents for synthesis and catalysis, *Chem. Rev.*, 99(1999) 2071–2083.
- [48] Sheng Dai, Yongkoo Seol, Shan Wickramanayake, David Hopkinson, Characterization of hollow fiber supported ionic liquid membranes using micro focus X-ray computed tomography, *Journal of Membrane Science*, 492(2015) 497–504.
- [49] C. Erkey, Supercritical carbon dioxide extraction of metal ions from aqueous solutions: a review, *Journal of Supercritical Fluids* 17 (2000) 259–287.

- [50] G. Afrane, E.H. Chimowitz, Experimental investigation of a new supercritical fluid inorganic membrane separation process, *Journal of Membrane Science*, 116(1996), 293–299.
- [51] S. Sarrade, C. Guizard, G.M. Rios, Membrane technology and supercritical fluids: chemical engineering for coupled processes, *Desalination*, 144 (2002), 137–142.
- [52] S. Bocquet, J. Romero, J. Sanchez, G.M. Rios, Membrane contactors for the extraction process with subcritical carbon dioxide or propane: simulation of the influence of operating parameters, *Journal of Supercritical Fluids*, 41 (2007) 246–256.
- [53] Y.J. Wang, Y. Wang, F. Chen, G.S. Luo, Y.Y. Dai, Mass transfer characteristics of cadmium(II) extraction in hollow fiber modules, *Chemical Engineering Science*, 58 (2003) 3223–3231.
- [54] K. Soldenhoff, M. Shamieh, A. Manis, Liquid–liquid extraction of cobalt with hollow fiber contactor, *Journal of Membrane Science*, 252 (2005)183–194.
- [55] Parisa Zaheria, Toraj Mohammadic, Hossein Abolghasemia, Mohammad Ghannadi Maraghe, Supported liquid membrane incorporated with carbon nanotubes for the extraction of Europium using Cyanex272 as carrier, *Chemical Engineering Research and Design*, 100(2015) 81–88.
- [56] R.A. Bartsch, J. Way (Eds.), *Chemical Separation with Liquid Membranes*, ACS Symposium Series 642, Amer. Chem. Soc, Washington, DC, 1996.
- [57] J. Robinson, M. Sims, Method and system for extracting a solute from a fluid using dense gas and a porous membrane, U.S. Patent 5,490,884, 1996.
- [58] M. Sims, Porocritical fluid extraction from liquids using near-critical fluids, *Membrane Technology*, 97(1998) 11–12.
- [59] H. Estay, Modeling and simulation of the mass transfer and selectivity of membrane contactor systems using supercritical fluids. Master Thesis, Chemical Engineering, University of Santiago de Chile, 2005.
- [60] H. Estay, S. Bocquet, J. Romero, J. Sanchez, G. Rios, F. Valenzuela, Modeling and simulation of mass transfer in near-critical extraction using a hollow fiber membrane contactor, *Chemical Engineering Science*, 62 (21) (2007), 5794–5808.
- [61] M. Lurdes F. Gameiro, M. Rosinda C. Ismael, M. Teresa A. Reis, Jorge M.R. Carvalho, Recovery of copper from ammoniacal medium using liquid membranes with LIX 54, *Separation and Purification Technology*, 63 (2008), 287–296.
- [62] Anil Kumar, R. Haddad, F.J. Alguacil, A.M. Sastre, Comparative performance of non-dispersive solvent extraction using a single module and the integrated membrane process with two hollow fiber contactors, *Journal of Membrane Science*, 248(2005), 1–14.

- [63]. S.F. Shen, K.H. Smith, S. Cook, S.E. Kentish, J.M. Perera, T. Bowser, G.W. Stevens, Phenol recovery with tributyl phosphate in a hollow fiber membrane contactor: Experimental and model analysis, *Separation and Purification Technology*, 69(2009), 48–56.
- [64] Jia-Jan Guo, Chii-Dong Ho, Jr-Wei Tu, Modeling extraction separation of Cu (II) in hollow-fiber modules, *Chemical Engineering Science*, 64 (2009) 3455 - 3465 .
- [65] P. Kazemi, M. Peydayesh, A. Bandegi, T. Mohammadi, O. Bakhtiari, Stability and extraction study of phenolic waste water treatment by supported liquid membrane using tributylphosphate and sesame oil as liquid membrane, *chemical engineering research and design*, 92 (2014)375–383.
- [66] N. L. Dudwadkar, S.C. Tripathi, P.S. Dhami and P.M. Gandhi, Partitioning of actinides from high level liquid waste employing supported liquid membrane technique using TOPO in n-dodecane as carrier, *Desalination and Water Treatment*, 52 (2014) 4755-4761.
- [67] P.C. Rout, K. Sarangi, A comparative study on extraction of Mo(VI) using both solvent extraction and hollow fiber membrane technique, *Hydrometallurgy*, 133(2013)149–155.
- [68] Prashant Praveen, Kai-Chee Loh, Simultaneous extraction and biodegradation of phenol in a hollow fiber supported liquid membrane bioreactor, *Journal of Membrane Science*, 430 (2013), 242–251.
- [69] Thanaporn Wannachod, Natchanun Leepipatpiboon, Ura Pancharoen, Kasidit Nootong, Separation and mass transport of Nd (III) from mixed rare earths via hollow fiber supported liquid membrane: Experiment and modeling, *Chemical Engineering Journal*, 248 (2014) 158–167.
- [70] Luciana de Souza Moraes , Frederico de Araujo Kronemberger, Helen Conceicao Ferraz, Alberto Claudio Habert, Liquid–liquid extraction of succinic acid using a hollow fiber membrane contactor, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 206-211.
- [71]. A.K. Pabby, J.V. Sonawane, A.M. Sastre and Y. Kulkarni, Industrial Applications of Membrane Contactors, in: A.K. Pabby, S.S.H. Rizvi, A.M. Sastre (eds.), *Hand Book of Membrane Separations: Chemical, Pharmaceutical Food and Biotechnological Application*, Second Edition, CRC Press, Boca Raton, FL, (Chapter 4), 2015: 53-76,.
- [72] Anil Kumar, R. Haddad, G. Benzal, R. Ninou, A.M. Sastre, Use of modified membrane carrier system for recovery of gold cyanide from alkaline cyanide media using hollow fiber supported liquid membranes: feasibility studies and mass transfer modeling, *Journal of Membrane Science*, 174 (2000) 17–30.
- [73] A.K. Pabby, R. Haddad, F.J. Alguacil and A.M. Sastre, Improved kinetics-based gold cyanide extraction with mixture of LIX79 + TOPO utilizing hollow fiber membrane contactors *Chem. Eng. J.*, 100 (2004) 11-22.

- [74] A.G. Gaikwad and A.M. Rajput, Transport of yttrium metal ions through fibers supported liquid membrane solvent extraction, *J. Rare Earths*, 28 (2010)1-6.
- [75] S. Panja, R.Ruhela, A.Das, S.C.Tripathi, A.K.Singh, P.M.Gandhi, R.C.Hubli, Carrier mediated transport of Pd(II) from nitric acid medium using Dithiodiglycolamide (DTDGA) across a supported liquid membrane (SLM), *Journal of Membrane Science*, 449 (2014) 67–73.
- [76] R. Ruhela, J.N.Sharma, B.S.Tomar, S.Panja, S.C.Tripathi, R.C.Hubli, A.K.Suri, N, N, N', N'-tetra(2-ethylhexyl)thiodiglycolamide T(2EH)TDGA: a novel ligand for the extraction of palladium from high level liquid waste (HLLW), *Radiochimica Acta.*, 98 (2010)209–214.
- [77] Zisu Hao, Michael E. Vilt, Zihao Wang, Weidong Zhang, W.S.Winston Ho, Supported liquid membranes with feed dispersion for recovery of Cephalexin, *Journal of Membrane Science*, 468(2014) 423–431.
- [78] Zisu Hao, Zihao Wang, Weidong Zhang, W.S.Winston Ho, Supported liquid membranes with organic dispersion for recovery of Cephalexin, *Journal of Membrane Science*, 468 (2014), 90–97.
- [79] N.S. Rathore, A. Leopold, A.K. Pabby, A. Fortuny, M.T. Coll and A.M. Sastre, Extraction and permeation studies of Cd(II) in acidic and neutral chloride media using Cyanex 923 on supported liquid membrane, *Hydrometallurgy*, 96(2009), 81-87.
- [80] Ayça Hasanoğlu, Removal of phenol from wastewaters using membrane contactors: Comparative experimental analysis of emulsion pertraction, *Desalination*, 309 (2013) 171–180.
- [81] Francisco Jose Alguacil, Irene Garcia-Diaz, Felix Lopez, Ana Maria Sastre, Cobalt(II) membrane-extraction by DP-8R/Exxsol D100 using pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) processing, *Separation and Purification Technology*, 80(2011) 467–472
- [82] Smita Gupta, Mousumi Chakraborty, Z.V.P. Murthy, Optimization of process parameters for mercury extraction through pseudo-emulsion hollow fiber strip dispersion system, *Separation and Purification Technology*, 114 (2013) 43–52.
- [83] A. Mondal, S. Ghosh, A. Bhowal, and S. Datta, Vanadium Extraction using Pseudo-Emulsion Based Hollow-Fiber with Strip Dispersion Technique, *Separation Science and Technology*, 48 (2013) 877–883.
- [84]. Shiva Agarwal, M. Teresa A. Reis, M. Rosinda C. Ismael, M. Joana N. Correia, Jorge M.R. Carvalho, Application of pseudo-emulsion based hollow fibre strip dispersion (PEHFSD) for the recovery of copper from sulphate solutions, *Separation and Purification Technology*, 102 (2013)103–110.

- [85] Shiva Agarwal, M. Teresa A. Reis, M. Rosinda C. Ismael, Jorge M.R. Carvalho, Zinc extraction with Ionquest 801 using pseudo-emulsion based hollow fibre strip dispersion technique, *Separation and Purification Technology*, 127 (2014)149–156.
- [86] F.J. Alguacil, M. Alonso, F.A. Lopez, and A. Lopez-Delgado, Transport of $\text{Au}(\text{CN})_2^-$ by mixtures of amine primene JMT and phosphine oxide CYANEX 923 using the pseudo-emulsion based hollow-fiber strip dispersion technology, *Solvent Extraction and Ion Exchange*, 30(2012) 54–66.
- [87] Xiaojian Luo, Dingsheng He, and Ming Ma, Simultaneous Transport and Separation of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ in Cu-Zn-Co Sulfate Solution by Double Strip Dispersion Hybrid Liquid Membrane (SDHLM), *Separation Science and Technology*, 45 (2010) 2130–2140.
- [88] E. Bringas, M.F. San Román, A.M. Urriaga, I. Ortiz, Integrated use of liquid membranes and membrane contactors: Enhancing the efficiency of L-L reactive separations, *Chemical Engineering and Processing: Process Intensification*, *Chemical Engineering and Processing*, 67 (2013)120– 129.
- [89]. A.K. Pabby, S.C. Roy, J.V. Sonawane, N.S. Rathore, C.B. Patil, A.M. Sastre and Y. Kulkarni, Hollow-Fiber Renewal and Strip Dispersion Liquid Membrane Techniques: Application for Metal Separation, Recovery, and Wastewater Treatment, in: A.K. Pabby, S.S.H. Rizvi, A.M. Sastre (eds.), *Hand Book of Membrane Separations: Chemical, Pharmaceutical Food and Biotechnological Application*, Second Edition, CRC Press, Boca Raton, FL, (Chapter 32), 2015: 813-823.
- [90] Agustin Fortuny, Maria Teresa Coll, Ana Maria Sastre, Ionic liquids as a carrier for chloride reduction from brackish water using hollow fiber renewal liquid membrane, *Desalination*, 343 (2014)54–59.
- [91]Zhongqi Ren, Huilin Meng, Weidong Zhang, Junteng Liu,and Chunhua Cui, The Transport of Copper(II) through Hollow Fiber Renewal Liquid Membrane and Hollow Fiber Supported Liquid Membrane, *Separation Science and Technology*, 44 (2009) 1181–1197.
- [92] Hugo Valdés, Rossana Sepúlveda, Julio Romero, Fernando Valenzuela, José Sánchez, Near critical and supercritical fluid extraction of $\text{Cu}(\text{II})$ from aqueous solutions using a hollow fiber contactor, *Chemical Engineering and Processing*, 65(2013)58– 67.
- [93] Saeed Shirazian, Azam Marjani, Farzad Fadaei. Supercritical extraction of organic solutes from aqueous solutions by means of membrane contactors: CFD simulation, *Desalination*, 277 (2011) 135–140.
- [94] F.J. Alguacil, I. Garcia-Diaz, F.A. Lopez, . Modeling of facilitated transport of $\text{Cr}(\text{III})$ using $(\text{RNH}_3^+ \text{HSO}_4^-)$ ionic liquid and pseudo-emulsion hollow fiber strip dispersion (PEHFSD) technology, *Journal of Industrial and Engineering Chemistry*, 19 (2013)1086–1091.

- [95] Olga C. Vangeli, George E. Romanos,, Konstantinos G. Beltsios , Demosthenes Fokas, Chrysoula P. Athanasekou, Nick K. Kanellopoulos Development and characterization of chemically stabilized ionic liquid membranes-Part I: Nanoporous ceramic supports, *Journal of Membrane Science*, 365 (2010)366–377.
- [96] Antonia P. de los Rios, Francisco J. Hernandez-Fernandez, Hugo Presa Demetrio Gomez, Gloria Villora, Tailoring supported ionic liquid membranes for the selective separation of transesterification reaction compounds, *Journal of Membrane Science*, 328 (2009) 81–85.
- [97] F.J. Hernandez, A.P. de los Rios, M. Rubio, F. Tomas-Alonso, D. Gomez, G. Villora, A novel application of supported liquid membranes based on ionic liquids to the selective simultaneous separation of the substrates and products of a transesterification reaction, *J. Membr. Sci.*, 293(2007) 73–80.
- [98] Li-Hua Cheng, Muhammad Syukri Abd Rahaman, Ru Yao, Lin Zhang, Xin-Hua Xu, Huan-Lin Chen, Juin-Yih Lai , Kuo-Lun Tung, Study on microporous supported ionic liquid membranes for carbon dioxide capture, *International Journal of Greenhouse Gas Control*, 21(2014)82–90.
- [99] S. Nosrati, N.S. Jayakumar, M.A. Hashim, Performance evaluation of supported ionic liquid membrane for removal of Phenol, *Journal of Hazardous Materials*, 192(2011) 1283– 1290.
- [100] X.J. Yang, A.G. Fane, K. Soldenhoff, Comparison of liquid membrane processes for metal separations: permeability, stability, and selectivity, *Ind. Eng. Chem. Res.*, 42(2003) 392–403.
- [101] Y. Qian, Copper recovery and spent etchant regeneration based on supported liquid membrane technology, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, 2007.
- [102] Y. Wang, Y.S. Thio, F.M. Doyle, Formation of semi-permeable polyamide skin layers on the surface of supported liquid membranes, *J. Membr. Sci.*, 147(1998) 109–116.
- [103] C. Fabiani, M. Merigiola, G. Scibona, A.M. Castagnola, Degradation of supported liquid membranes under an osmotic pressure gradient, *J. Membr. Sci.*, 30(1987) 97–104.
- [104] P.R. Danesi, L. Reichley-yinger, P.G. Rickert, Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the long term stability of the membranes, *J. Membr. Sci.*, 31(1987)117–145.
- [105] A.M. Neplenbroek, D. Bargeman, C.A. Smolders, Supported liquid membranes: instability effects, *J. Membr. Sci.*, 67(1992) 121–132.
- [106] F.F. Zha, A.G. Fane, C.J.D. Fell, Instability mechanisms of supported liquid membranes in phenol transport process, *J. Membr. Sci.*, 107(1995)59–74.

- [107] H. Zheng, B. Wang, Y. Wu, Q. Ren, Instability mechanisms of supported liquid membrane for phenol transport, *Chin. J. Chem. Eng.*, 17(2009) 750–755.
- [108] Gabriel Zarca, Inmaculada Ortiz, Ane Urtiaga, Copper(I)-containing supported ionic liquid membranes for carbon monoxide/nitrogen separation, *Journal of Membrane Science*, 438(2013), 38–45.
- [109] A. I. Labropoulos, G. Em. Romanos, E. Kouvelos, P. Falaras, V. Likodimos, M. Francisco, M. C. Kroon, B. Iliev, G. Adamova, and Thomas J. S. Schubert., Alkyl-methylimidazolium Tricyanomethanide Ionic Liquids under Extreme Confinement onto Nanoporous Ceramic Membranes, *J. Phys. Chem. C*, 117(2013)10114–10127.
- [110] Wenjie Lan, Shaowei Li, Jianhong Xu, and Guangsheng Luo, Preparation and Carbon Dioxide Separation Performance of a Hollow Fiber Supported Ionic Liquid Membrane Wenjie Lan, Shaowei Li, Jianhong Xu, and Guangsheng Luo, *Ind. Eng. Chem. Res.* 52 (2013) 6770–6777.
- [111] Santos, J. Albo, C.I. Daniel, C.A.M. Portugal, J.G. Crespo, A. Irabien, Permeability modulation of Supported Magnetic Ionic Liquid Membranes (SMILMs) by an external magnetic field *Journal of Membrane Science* 430 (2013) 56–61.
- [112] E. Santos, J. Albo, A. Irabien, Acetate based Supported Ionic Liquid Membranes (SILMs) for CO₂ separation : Influence of the temperature, *Journal of Membrane Science*, 452 (2014) 277–283.
- [113] Jonathan Castillo, María Teresa Coll, Agustín Fortuny, Patricio Navarro Donoso, Rossana Sepúlveda, Ana María Sastre, Cu(II) extraction using quaternary ammonium and quaternary phosphonium based ionic liquid, *Hydrometallurgy*, 141 (2014) 89–96.
- [114] S. Venkatesan, K.M. Meera Sheriffa Begum, Emulsion liquid membrane pertraction of benzimidazole using a room temperature ionic liquid (RTIL) carrier, *Chemical Engineering Journal*, 148 (2009)254–262.
- [115] Shan Wickramanayake, David Hopkinson, Christina Myers, LangSui, David Luebke, Investigation of transport and mechanical properties of hollow fiber membranes containing ionic liquids for pre-combustion carbon dioxide capture, *Journal of Membrane Science*, 439 (2013)58–67.
- [116] Lizhe Liang, Quan Gan, Paul Nancarrow, Composite ionic liquid and polymer membranes for gas separation at elevated temperatures, *Journal of Membrane Science*, 450(2014), 407–417.
- [117] Matthew Zeh, Shan Wickramanayake and David Hopkinson, Failure Mechanisms of Hollow Fiber Supported Ionic Liquid Membranes, *Membranes*, 6 (2016) 21-32.
- [118] Kuan Huang, Xiao-Min Zhang, Ya-Xin Li, You-Ting Wu, Xing-Bang Hu, Facilitated separation of CO₂ and SO₂ through supported liquid membranes using carboxylate-based ionic liquids, *Journal of Membrane Science*, 471 (2014)227–236.
- [119] X.B. Hu, Y.X. Li, K. Huang, S.L. Ma, H. Yu, Y.T. Wu, Z.B. Zhang, Impact of alpha-D-glucose pentaacetate on the selective separation of CO₂ and SO₂ in supported ionic liquid membranes, *Green Chem.*, 14 (2012)1440–1446.

- [120] Ana R. Ferreira, Luísa A. Neves, Jorge C. Ribeiro, Fernando M. Lopes, João A.P. Coutinho, Isabel M. Coelho, João G. Crespo, Removal of thiols from model jet-fuel streams assisted by ionic liquid membrane extraction, *Chemical Engineering Journal*, 256 (2014) 144–154.
- [121]. Spas D. Kolev, M. Inês G.S. Almeida, and Robert W. Cattrall, Polymer Inclusion Membranes, in: A.K. Pabby, S.S.H. Rizvi, A.M. Sastre (eds.), *Hand Book of Membrane Separations: Chemical, Pharmaceutical Food and Biotechnological Application*, Second Edition, CRC Press, Boca Raton, FL, 2015, pp. 723-740, Chapter 27.
122. Seraj A. Ansari, Pankaj Kandwal, and Prasanta K. Mohapatra, Liquid Membranes for Studies Involving Nuclear Waste Remediation Using Hollow-Fiber Contactors in: A.K. Pabby, S.S.H. Rizvi, A.M. Sastre (eds.), *Hand Book of Membrane Separations: Chemical, Pharmaceutical Food and Biotechnological Application*, Second Edition, CRC Press, Boca Raton, FL, 2015, pp. 787-808, Chapter 31.
123. A. K. Pabby and A.M. Sastre, Membrane techniques in analytical applications: Developments and advances. in *Encyclopedia of Analytical Chemistry*. Edited by Robert Meyers and Zeev Alfassi, John Wiley, New York, USA, Vol 13, 2009, 1-34.
- [124] Ahmet Kaya, Hamza Korkmaz Alpoguz, and Aydan Yilmaz, Application of Cr(VI) Transport through the Polymer Membrane with a New Synthesized Calix[4]arene Derivative, *Ind. Eng. Chem. Res.* 52(2013) 5428–5436.
- [125] Alexander M. St John, Robert W. Cattrall, Spas D. Kolev Extraction of uranium(VI) from sulfate solutions using a polymer inclusion membrane containing di-(2-ethylhexyl) phosphoric acid *Journal of Membrane Science*, 364(2010) 354–361.
- [126] M.I. Vázquez a, V.Romero a, C.Fontàs b, E.Anticó b, J.Benavente Polymer inclusion membranes (PIMs) with the ionic liquid (IL) Aliquat 336 as extractant: Effect of base polymer and IL concentration on their physical–chemical and elastic characteristic, *Journal of Membrane Science*, 455(2014) 312–319.
- [127] Omar Arousa, Mourad Amara, Mohamed Trari, Aissa Bouguelia, Hacene Kerdjoudj, Cadmium (II) and lead (II) transport in a polymer inclusion membrane using tributyl phosphate as mobile carrier and CuFeO₂ as a polarized photo electrode, *Journal of Hazardous Materials*, 180 (2010) 493–498.
- [128] Flora E Mercader-Trejo, a Eduardo Rodríguez de San Miguel and Josefina de Gyves, Mercury(II) removal using polymer inclusion membranes containing Cyanex 471X, *J Chem Technol Biotechnol*, 84(2009) 1323–1330.
- [129] P.K. Mohapatra, D.S. Lakshmi, A. Bhattacharyya, V.K. Manchanda, Evaluation of polymer inclusion membranes containing crown ethers for selective cesium separation from nuclear waste solution, *Journal of Hazardous Materials*, 169 (2009) 472–479.

- [130] Beata Pospiech, Synergistic solvent extraction and transport of Zn(II) and Cu(II) across polymer inclusion membranes with a Mixture of TOPO, and Aliquat 336, *Separation Science and Technology*, 49 (2014) 1706–1712.
- [131] Beata Pospiech, Selective recovery of cobalt(II) towards lithium(I) from chloride media by transport across polymer inclusion membrane with triisooctylamine, *Polish Journal of Chemical Technology*, 16 (2014) 15-20.
- [132] Piotr Gajewski, Marta Przewozna, and Mariusz B. Bogacki, Influence of Carrier Concentration (1-Alkylimidazols and TOA) on Citric Acid Transport across Polymer Inclusion Membranes (PIM), *Separation Science and Technology*, 49 (2014), 1736–1744.
- [133]. Wódzki, R.; Nowaczyk, W. Membrane transport of organics. II. Permeation of some carboxylic acids through strongly basic polymer membrane. *J. Appl. Polym. Sci.*, 71(1999) 2179–2190.
- [134] B.N. Mahantya, D.R. Raut, P.K. Mohapatra, D.K. Dasa, P.G. Behere, Md. Afzal, Comparative evaluation of actinide ion uptake by polymer inclusion membranes containing TODGA as the carrier extractant, *Journal of Hazardous Materials*, 275(2014)146–153.
- [135] M.P. Jensen, T. Yaita, R. Chiarizia, Reverse-micelle formation in the partitioning of trivalent f-element cations by biphasic systems containing a tetraalkyldiglycolamide, *Langmuir*, 23(2007)4765–4774.
- [136] Aulia Indah Pratiwi, Takehiro Sato, Michiaki Matsumoto and Kazuo Kondo, Permeation Mechanism of Succinic Acid through Polymer Inclusion Membranes with Ionic Liquid Aliquat 336, *Journal of Chemical Engineering of Japan*, 47(2014) 314–318.
- [137]. María Ramos-Payán, Rut Fernández-Torres, Juan Luis Pérez-Bernal, Manuel Callejón-Mochón, Miguel Ángel Bello-López, A novel approach for electromembrane extraction based on the use of silver nanometallic-decorated hollow fibers, *Analytica Chimica Acta*, 84(2014)7–11.
- [138] P Kandwal, S Dixit, S Mukhopadhyay, and P K Mohapatra, Mass transport modeling of CS(I) through hollow fiber supported liquid membrane containing calyx-[4]-bis (2,3-naphtho) crown-6 as the mobile carrier, *Journal of Chemical Engineering*, 174 (2011) 110-116.
- [139] P Kandwal, S A Ansari, and P K Mohapatra, A highly efficient supported liquid membrane system for near quantitative recovery of radio-strontium from acidic feeds. PartII: Scale up mass transfer modeling in hollow fiber configuration, *Journal of Membrane. Science*, 405-406 (2012) 85-91
- [140] Sira Suren, Thidart Wongsawa, Ura Pancharoen, and Anchaleeporn Waritswat Lothongkum, Uphill transport and mathematical model of Pb (II) from dilute synthetic lead- containing solutions across hollow fiber supported liquid membrane, *Journal of Chemical Engineering*, 191 (2012), 503.-511.

- [141] Niti Sunsandee, Natchanun Leepipatpiboon, Prakorn Ramakul, and Ura Pancharoen, The selective separation of (S)- AMLODIPINE VIA A HOLLOW FIBER SUPPORTED LIQUID MEMBRANE: Modeling and experiment verification, *Journal of Chemical Engineering*, 180 (2012), 299-308.
- [142] Y D Jagdale, P V Vernekar, A W Patwardhan, A V Patwardhan, S A Ansari, P K Mohapatra and V K Manchanda, Mathematical model for the extraction of metal ions using hollow fiber supported liquid membrane operated in a recycle mode, *Journal of Separation Science and Technology*, 48 (2013) 1-14.
- [143] Niti Sunsandee, Natchanun Leepipatpiboon, and Prakorn Ramakul, Selective enantioseparation of levocetizine via a hollow fiber supported liquid membrane and mass transfer prediction, *Korean Journal of Chemical Engineering*, 30(6)(2013), 1312-1320.
- [144] P V Vernekar, A W Patwardhan, A V Patwardhan, S A Ansari, P K Mohapatra and V K Manchanda, Mathematical model for the extraction of Neodymium from nitrate media using hollow fiber supported liquid membrane operated in a recycling mode, *Journal of Separation Science and Technology*, 48 (2013), 1003-1014.
- [145] Thanaporn Wannachod, Natchanun Leepipatpiboon, Ura Pancharoen, and Suphot Phatanasri, Mass transfer and selective separation of neodymium ions via a hollow fiber supported liquid membrane using PC88Aas extractant, *Journal of Industrial and Engineering Chemistry*, 21(2015)535-541.
- [146] Sretha Chaturabul, , Thanaporn Wannachod, , Natchanun Leepipatpiboon, Ura Pancharoen, and Soorathep Kheawhom, Mass transfer of simultaneous extraction and stripping of mercury (II) from petroleum produced water via HFSLM, *Journal of Industrial and Engineering Chemistry*, 21(2015)1020-1028.
- [147] Sretha Chaturabul, Wanchalerm Srirachat, Thanaporn Wannachod, Prakorn Ramakul, Ura Pancharoen, and Soorathep Kheawhom, Separation of mercury (II) from petroleum produced water via hollow fiber supported liquid membrane and mass transfer modeling, *Journal of Chemical Engineering*, 265 (2015), 34-46.
- [148] Sujay Biswas, P N Pathak, and S B Roy, Kinetic Modeling of Uranium permeation across a supported liquid membrane employing dinonyl phenyl phosphoric acid (DNPPA) as the carrier, *Journal of Industrial Engineering Chemistry*, 19 (2013), 547-553.
- [149] Somnuk Boributh, Suttichai Assabumrungrat, Navadol Laosiripojana, and Ratana Jiratananon, A modeling study on the effects of membrane characteristics and operating parameters on physical absorption of CO₂ by hollow fiber membrane contactor, *Journal of Membrane. Science* 380 (2011) 21-33.
- [150]. Soumik Boributh, Wichitpan Rongwong, Suttichai Assabumrungrat, Navadol Laosiripojana, Mathematical modeling and cascade design of hollow fiber membrane contactor for CO₂ absorption by monoethanolamine, *Journal of Membrane. Science*, 401-402 (2012) 175-189.

[151] D N Ambre, S A Ansari, M Anitha, P Kandwal, D K Singh, H Singh and P K Mohapatra, Non-dispersive solvent extraction of neodymium using hollow fiber contactor: Mass transfer and modeling studies, *Journal of Membrane Science*, 446(2013)106-112.

[152] Saeed Shirazian, Azam Marjani, and Farzad Fadaei, Supercritical extraction of Organic solute from aqueous solutions by means of membrane contactors: CFD simulation, *Journal of Desalination*, 277 (2011) 135-140.

FIGURE CAPTIONS

Fig. 1. Schematic description of pure diffusion-type process (a) and simple facilitated transport (b) in liquid membranes (A: target species; C: selective carrier; AC: complex between species A and carrier C) [88].

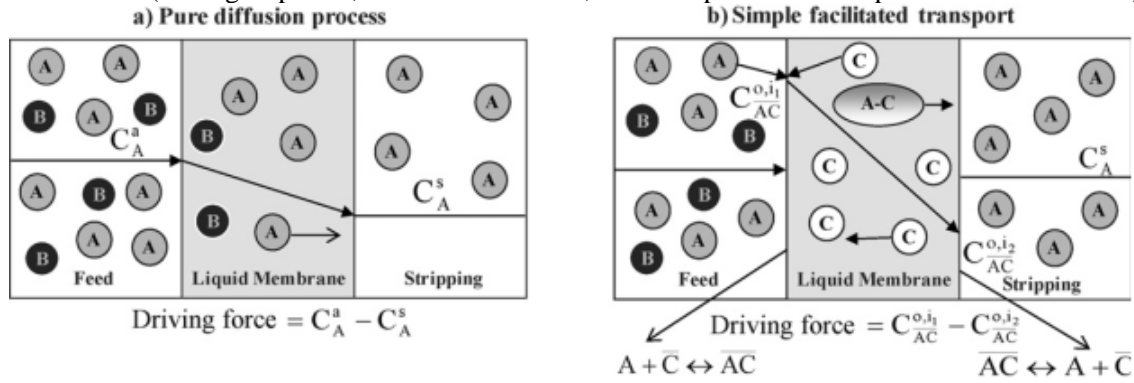


Fig. 2. Performance of the emulsion pertraction process [88].

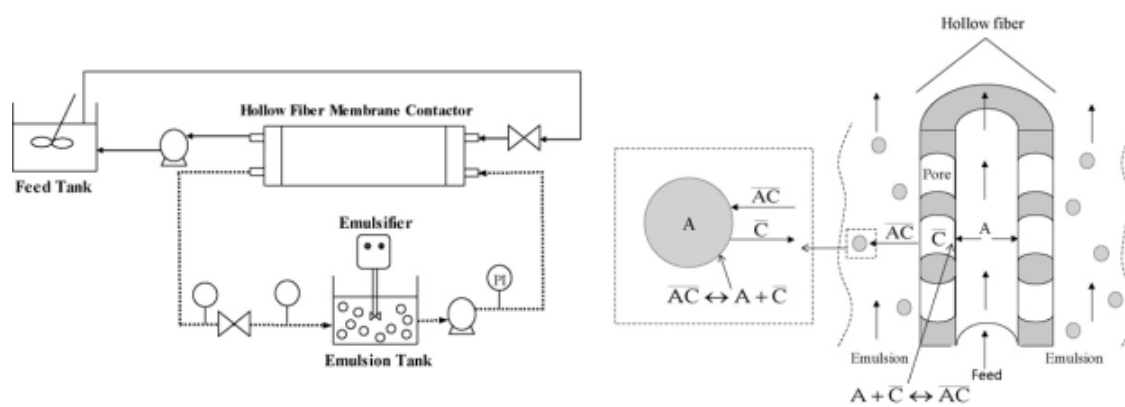


Fig. 3. (a) Schematic representation of the HFRLM process in single-pass mode, b) Principle of HFRLM process [28].

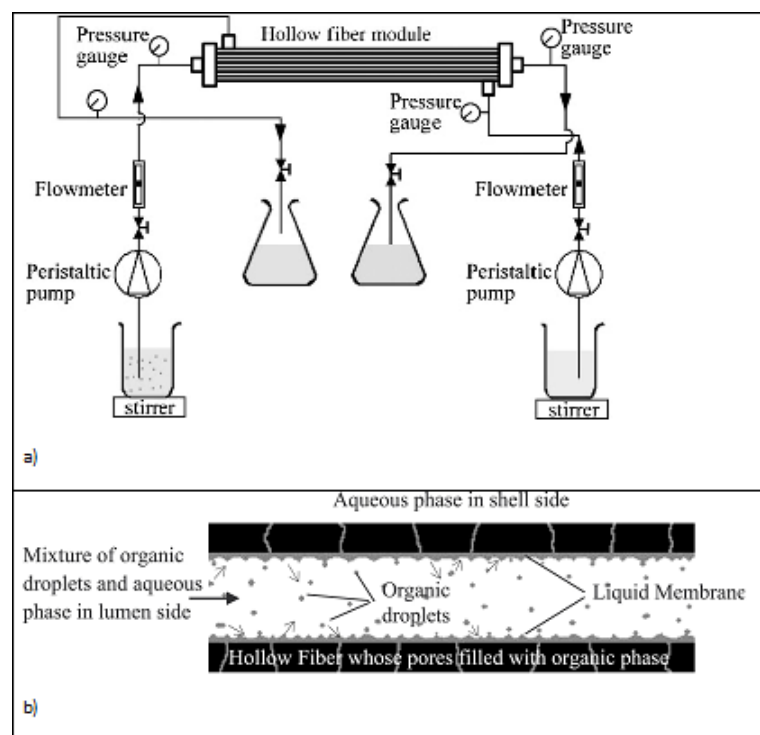


Fig. 4. Outline of the process studied in supercritical fluid (SCF) extraction: (a) circulation of the solutions inside and outside the hollow fiber, and (b) schematic representation of the mass transfer of metal ion M^{Z+} (Cu^{2+}) through the membrane. The figure shows the concentration profile of the cation M^{Z+} , the extractant compound A, and the complex $M(A)_z$ ($Cu(A)_2$) at the proximities of the membrane [92].

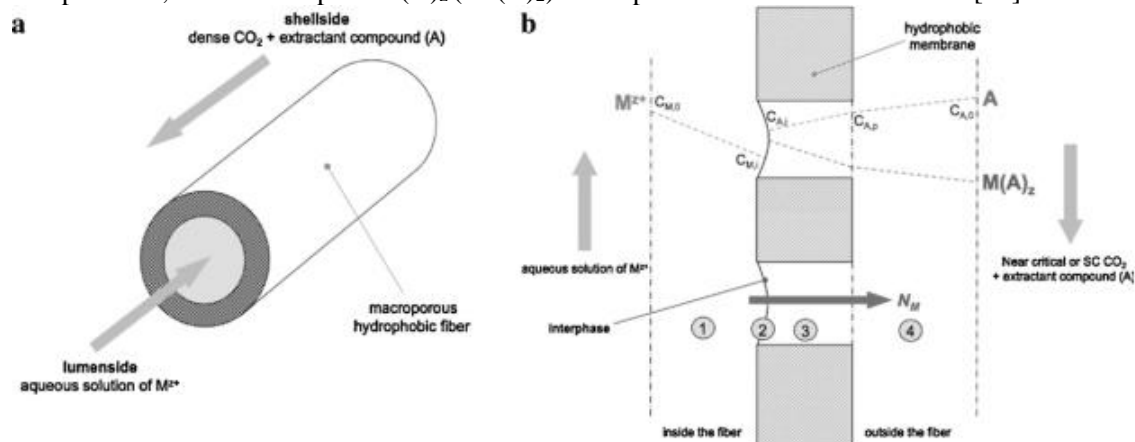


Fig. 5a. Schematic view of the membrane-based extraction process of Au(I) from cyanide media using a hollow fiber contactor: (1) hollow fiber contactor; (2,3) organic extractor and feed; (4) feed and organic pump; (5,6) inlet and outlet pressure gauge respectively for organic and feed; (7) flowmeters for feed and organic [62].

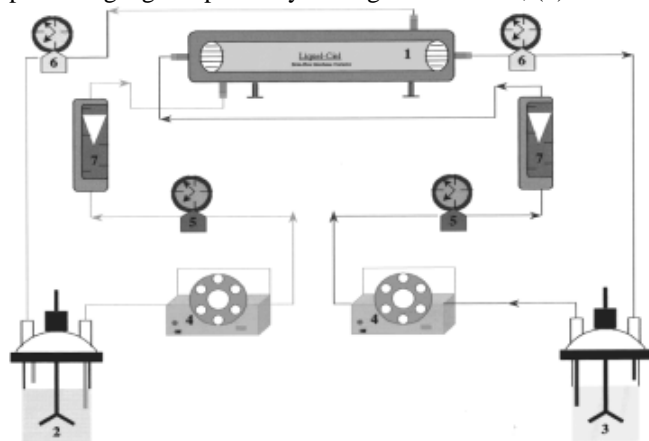


Fig. 5b. A schematic view of an integrated NdSX membrane process using two hollow fiber contactors. (1) feed phase reservoir tank, (2) pumps, (3) flow-meters, (4) extraction module, (5) organic phase, reservoir tank, (6) stripping module, (7) strip phase reservoir tank. Operation in counter-current and recirculation of the solutions [25]

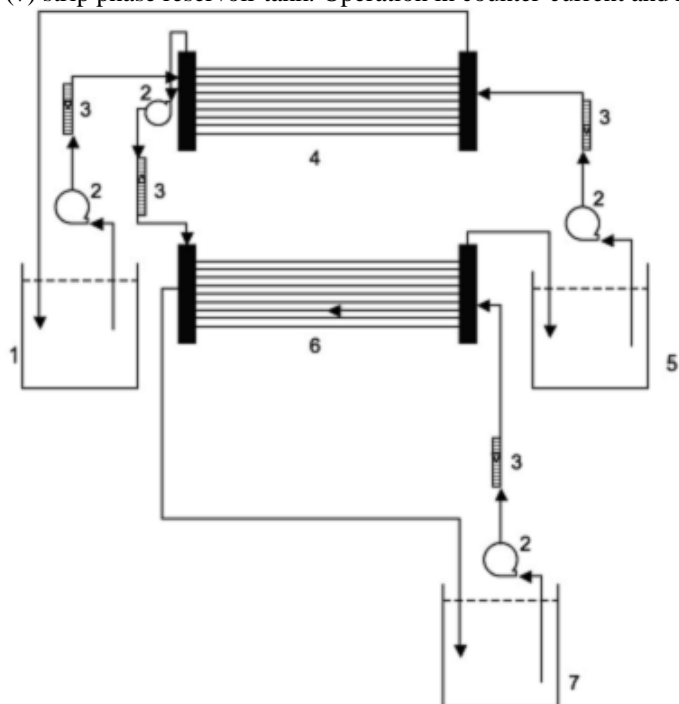


Fig. 6. Ionic liquids. a) 1-octyl-4-methylpyridinium cation, b) 1-octyl-3-methylimidazolium Cation [25].

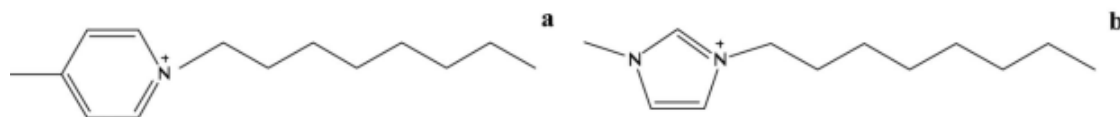


Fig. 7. Task selective ionic liquids. a) 1-salicylaldehyde-derived-4-methylimidazolium cation, b) 1-butyronitrile-4-methylpyridinium cation, c) 1-methyl-1-[4,5-bis(methylsulfide)] pentyloctadecinium cation [25].

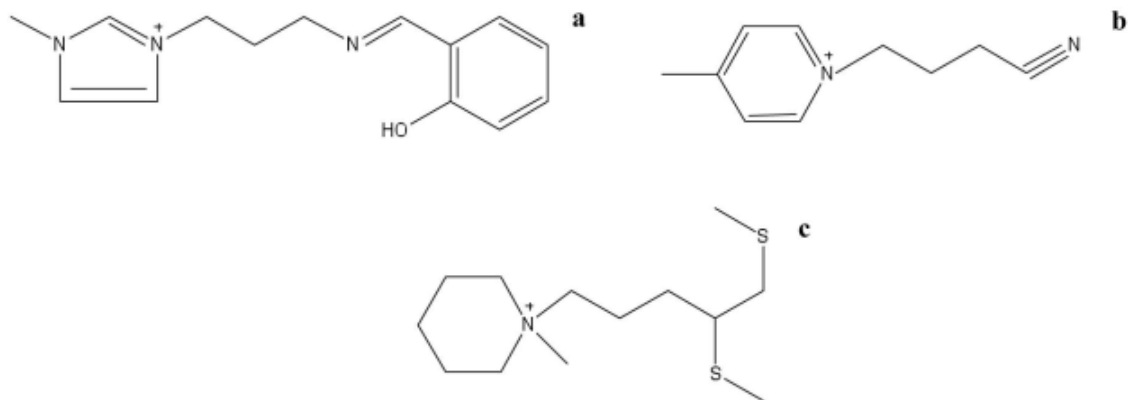


Fig. 8 Permeation of metal ions through liquid membrane with time. Experimental conditions: $[\text{Mo}]_{\text{Aq}}$: 10.75, $[\text{Cu}]_{\text{Aq}}$: 16.07, $[\text{Ni}]_{\text{Aq}}$:17.51, $[\text{Co}]_{\text{Aq}}$:17.27, $[\text{Zn}]_{\text{Aq}}$:15.66, $[\text{Fe}]_{\text{Aq}}$:18.27 and $[\text{Mn}]_{\text{Aq}}$:18.82 mol/m³, [Extractant]: 0.48 M, pH: 1.5, Flow rate: 420 mL/min, $[\text{NH}_4\text{OH}]$: 0.03 M [67].

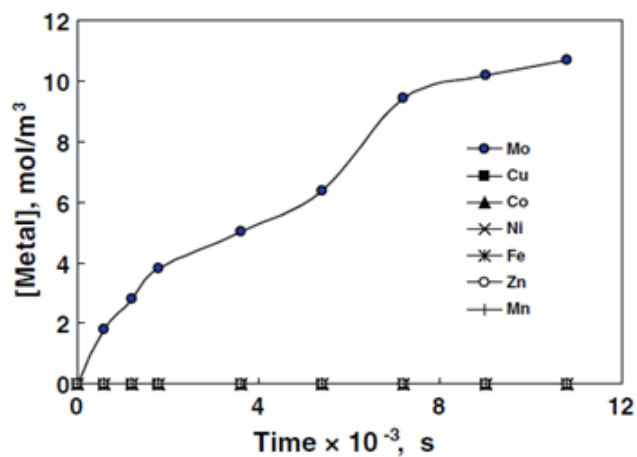


Fig. 9 Transport behavior of various elements using DTDGA as carrier; $[\text{HNO}_3]=4\text{ M}$, $[\text{DTDGA}]=0.025\text{ M}$, Stripant-0.01M Thiourea in 0.2M HNO_3 , Membrane-0.2 mm PTFE [75].

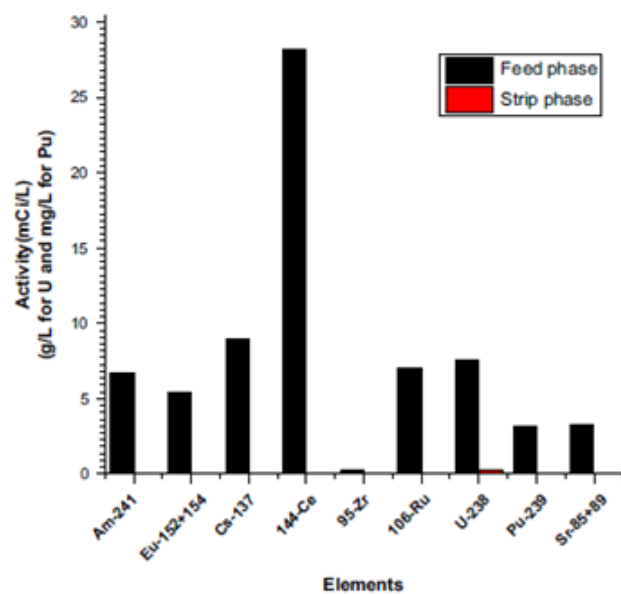


Fig. 10 A schematic diagrams of an enlarged view of the (a) SLM-feed dispersion (SLM-FD) process[77] (b) SLM-organic dispersion (SLM-OD) process [78].

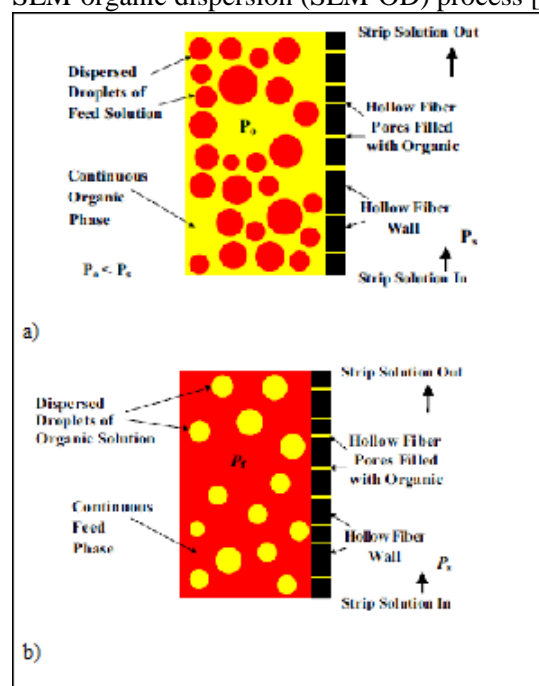


Fig. 11. The comparison of SLM-FD (FD) and solvent extraction (SX) for dimension- less Cephalixin concentration ($C_{f,0}=8$ mM; $C_{QCl,0}=2.5$ wt%; SLM-FD: $V_s=300$ ml, $C_{KCl}=1$ M, $Q_{fd}=200$ ml/min, $Q_s=400$ ml/min; Solvent extraction: $V_f=30$ ml) [77].

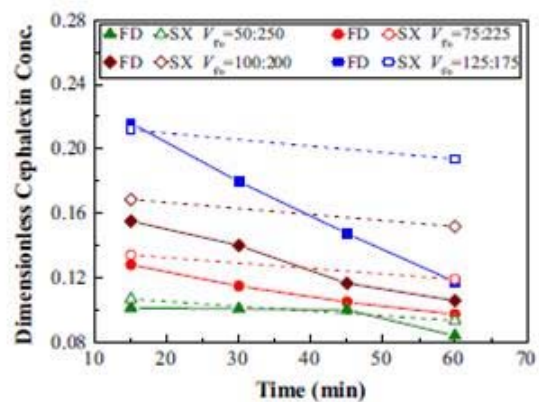


Fig. 12. Cephalixin concentrations in the feed and strip phases vs. time with varying KCl concentration ($C_{f0}=8$ mM, $V_f=500$ ml; $C_{QCl,0}=2.5$ wt%, $V_o=80$ ml; $V_s=500$ ml, $Q_{od}=200$ ml/min, $Q_s=400$ ml/min) [78].

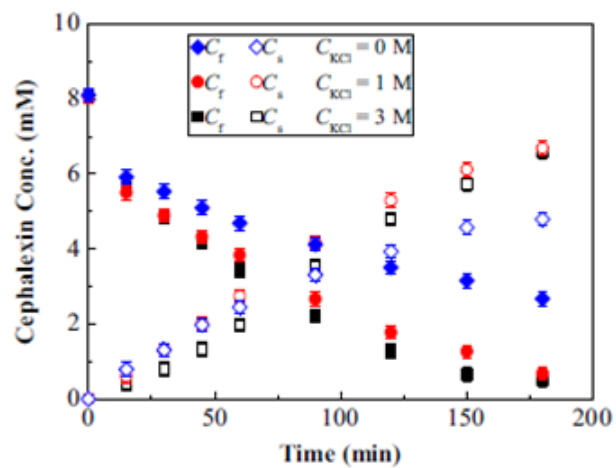


Fig. 13. Cephalixin concentrations in the feed and strip phases vs.time with varying the flow rates on the shell and lumen sides ($C_{f,0}$ 8 mM, $V_f=500$ ml; $C_{QCl,0}$ =2.5 wt %, $V_o=80$ ml; $V_s=500$ ml, $C_{KCl}=1$ M) [78].

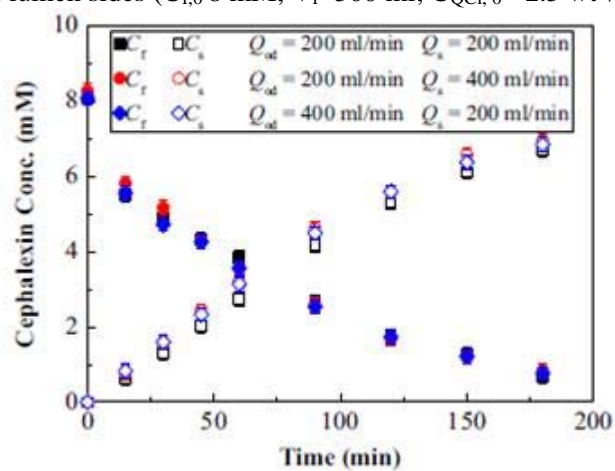


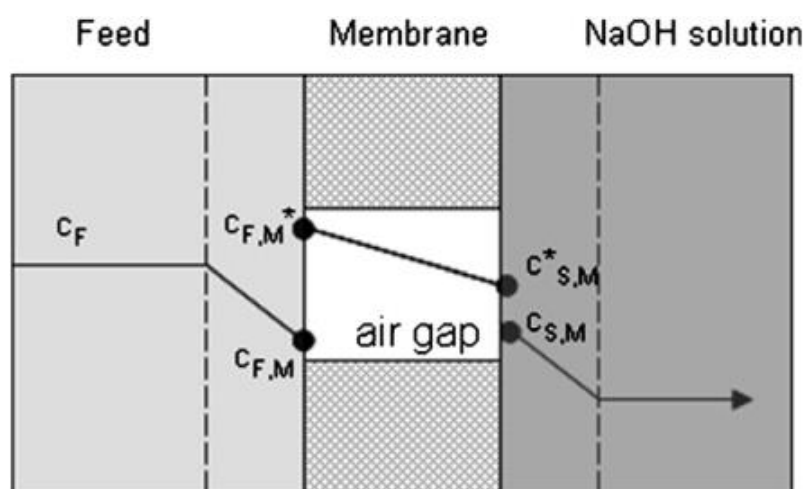
Fig. 14. Illustration of solute transfer by gas-filled membrane [80].

Fig. 15. Scheme of the strip dispersion hybrid liquid membrane used for performing transport experiments. 1. Feed phase compartment containing Cu^{2+} , Zn^{2+} , Co^{2+} , and SO_4^{2-} . 2. Compartment containing strip dispersion phase for extraction of Cu^{2+} . 3. Compartment containing strip dispersion phase for extraction of Zn^{2+} . 4. Supported liquid membrane for extraction of Cu^{2+} . 5. Supported liquid membrane for extraction of Zn^{2+} . 6. Mixer for mixture of organic solution and strip solution. 7. Pump for circulating flux. 8. Strip solution containing 3M HCl. 9. Strip solution containing 2M H_2SO_4 . 10. Organic solution impregnated in support pores [87].

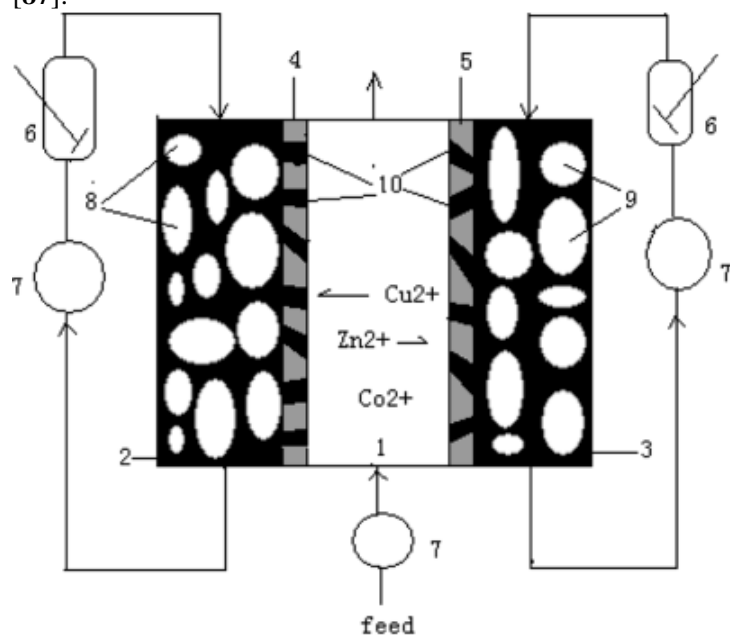


Fig. 16. Effect of dodecanol on the transport on Zn(II) and Cu(II) ion. For Cu(II), feed phase: $1.57 \times 10^{-3} \text{M Cu}^{2+}$, $0.167 \text{M Na}_2\text{SO}_4$, $\text{pH}=3.20$, circulating flux= 9900 ml/h . Strip dispersion system : 100 mL kerosene solution containing $10\% \text{ M5640 (w/v)}$, dodecanol of different concentration, and 20 mL 3M HCl strip solution. The circulating flux of strip dispersion system= 560 ml/h . For Zn(II), feed phase: $1.53 \times 10^{-3} \text{M Zn}^{2+}$, $0.167 \text{M Na}_2\text{SO}_4$, $\text{pH}=4.33$, and circulating flux= 5600 ml/h . strip dispersion system : 110 mL kerosene solution containing 0.4M dimer of HEH(EHP), dodecanol of different concentration and 10 mL $2 \text{M H}_2\text{SO}_4$ strip solution. The circulating flux of strip dispersion system = 560 ml/h [87].

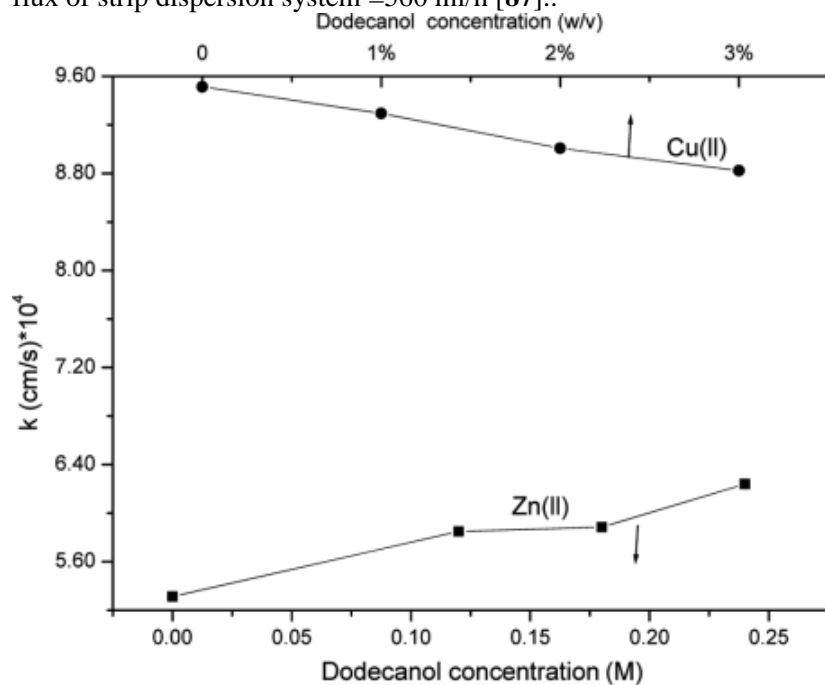


Fig.17.Effect of volume ratio (x) on transport. For Cu(II), the other experimental conditions are the same as Fig. 16 except for 3M HCl of different volume. For Zn(II), the other experimental conditions is the same as Fig. 16 except for 2M H₂SO₄ of different volume. The concentration of dodecanol is 0.24 M [87].

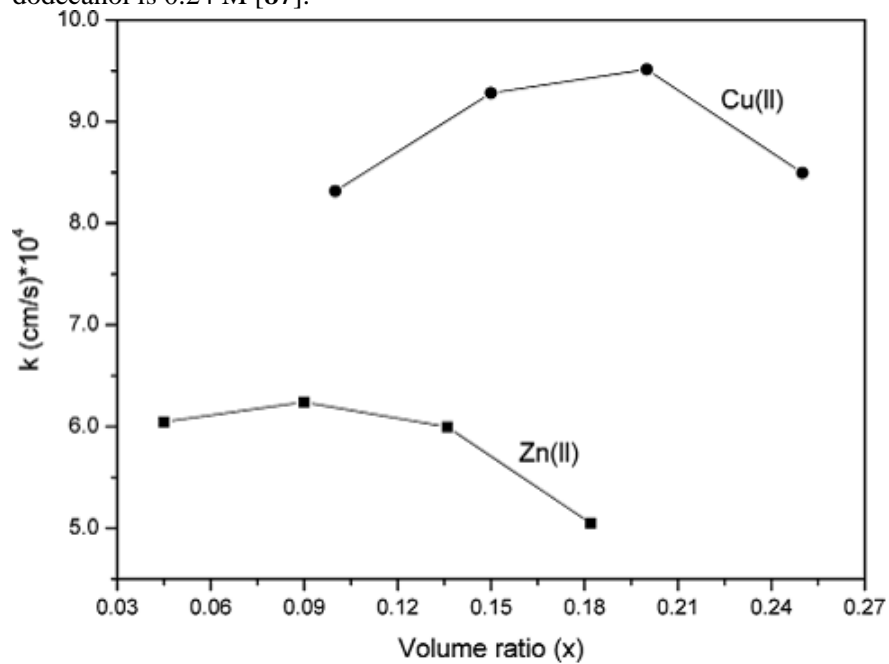


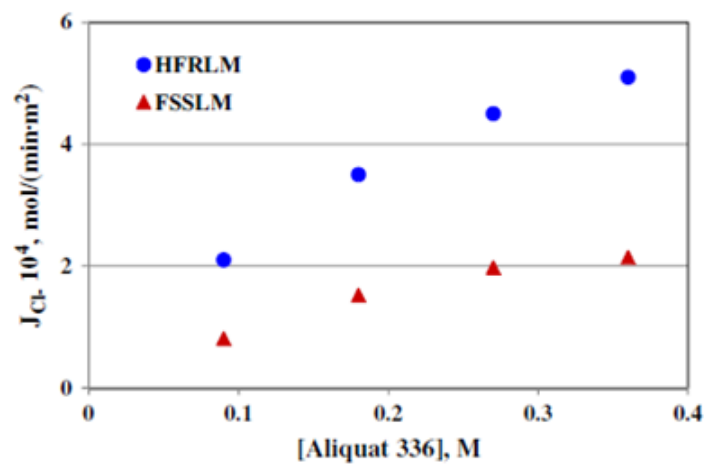
Fig. 18. Effect of the concentration of the carrier (Aliquat 336) on the chloride flux [90].

Fig. 19 CT scan images showing the location of the IL in the fiber: (a) fiber without IL;(b) uncleaned fiber saturated with IL and (c) fiber that was saturated with IL and subsequently cleaned [48].

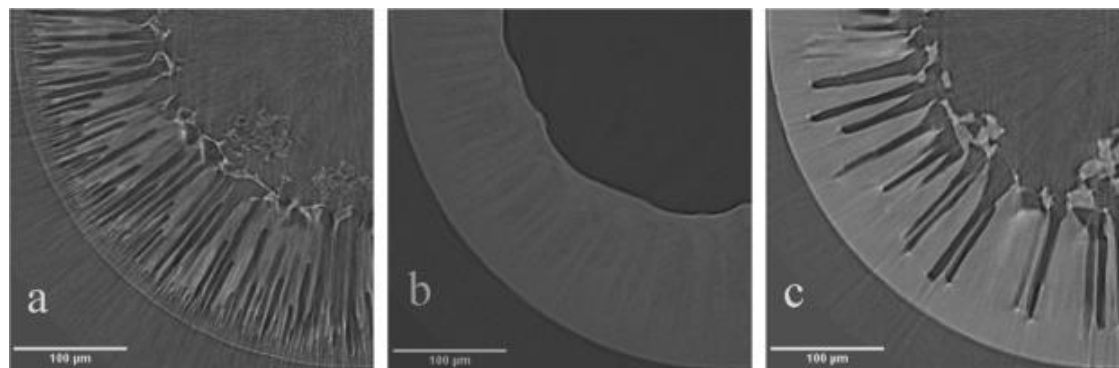


Fig.20 SILM ionic liquid loss along time, for the SILMs composed by PVDF

hydrophobic (full symbols) and hydrophilic (dotted symbols), with the ionic liquids [C₂mim][CF₃SO₃] (black symbols and solid line), [C₂mim][NTf₂] (grey symbols and dot-dashed line), and [C₂mim][MeSO₄] (white symbols and dashed line), for positive pressure differences of 0.5 bar (circles), 1.0 bar (squares), 1.4 bar (hexagons), 1.5 bar (diamonds), 1.6 bar (cross), 1.8 bar (inverse triangles), and 2.0 bar (triangles), using a nitrogen gas stream on the AmiconTH 8010 cell[120].

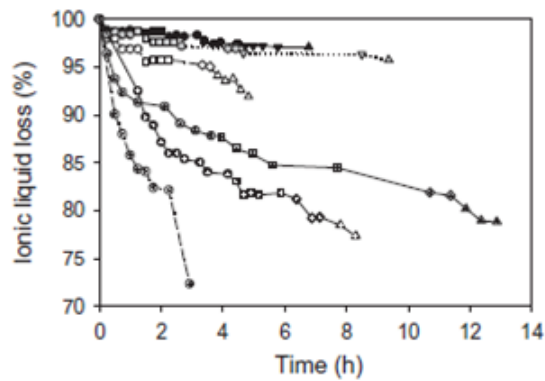


Fig. 21 Proposed mechanism (fixed-site jumping) of citric acid transport through polymer inclusion membrane [132].

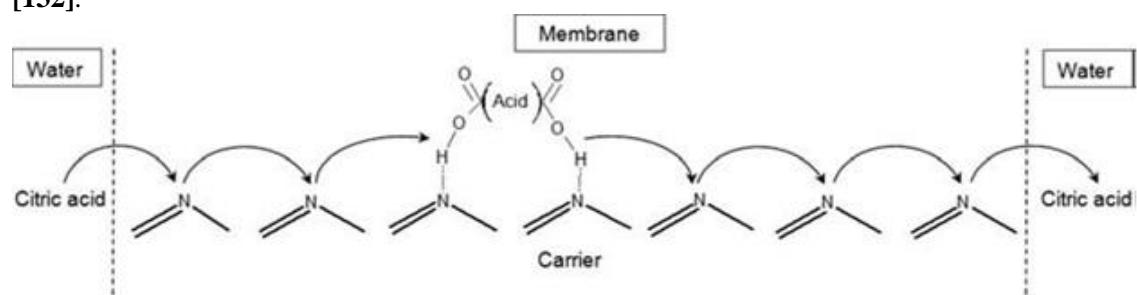


Fig. 22. The flux times thickness value ($J \cdot d$) vs. initial citric acid concentration in the feed phase for 1-alkylimidazoles as a carrier ($X = 0.49$). Receiving phase: demineralized water. Cellulose triacetate as polymer matrix[132].

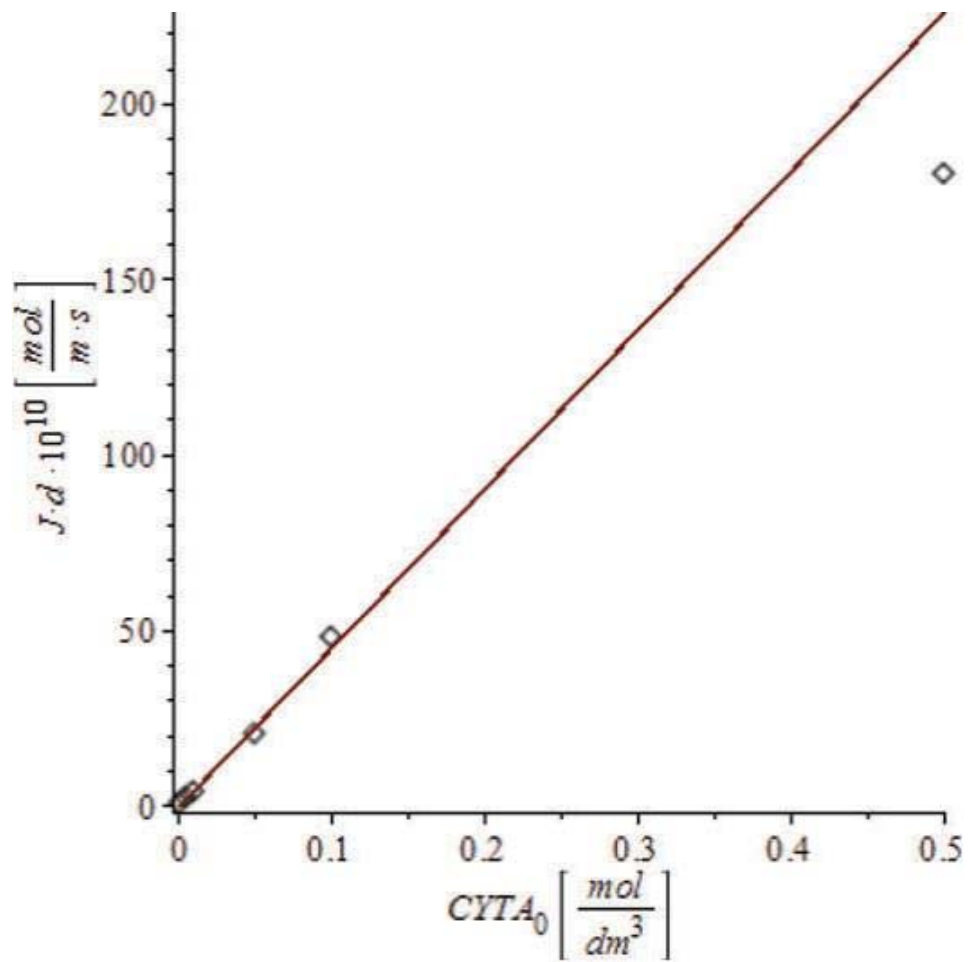


Table 1 Comparison of hollow fiber membrane and solvent extraction technique [Ref. 67].

Hollow fiber membrane technique	Solvent extraction technique
Both extraction and stripping were achieved in a single stage	Three stage extraction and two stage stripping were required
Only 13 mL of extractant was used for the continuous run of 4 L of feed solution.	Three liters of extractant was used for the continuous run of 4 L of feed solution
Mo recovery was 99.8%	Mo recovery was 84.43%
Solvent loss is negligible	Solvent loss is comparatively more
No crud formation	Some crud formation was observed with mixer-settler
No phase separation problem	Slight emulsion was observed during stripping
pH of feed solution can be adjusted	Difficult to adjust pH of feed solution because of multi stage operation
Small volume of solvent was consumed	Large volume of solvent was consumed

Table 2 Performance comparison of two phase partitioning bioreactors (TPPBs) in biodegradation of phenol [68]

Partitioning phase	Microorganism	Lag phase duration (h)	Phenolconc.(mg L⁻¹)	Removal time (h)
2-ndecanone	P. putida11,172	12	4000	60
2-ndecanone	P. putida F1	8	500	28
EVA	P. putida 11,172	13	2000	60
EVA	Microbial consortium	---	2000	30
Kerosene	P. putida 14,365	10	1800	80
Hytrel KNU417	P. fluorescence	10	2000	19
2-ndecanone	P. putida 11,172	0	2000	36

Table 3 Cobalt transport in presence of lithium using different acidic carriers (Ref 81).

Carrier	$K \times 10^5, \text{ cm s}^{-1}$	$\beta_{\text{Ca,Li}}$
DP-8R	4.4	22.0
Cyanex 272	2.4	18.5
Acorga PT5050	1.7	21.5

Feed phase: 1.7×10^{-4} M (each) Co(II) and Li(I) at pH 5.0. Pseudo-emulsion phase:
10% v/v carrier in Exxsol D100 + 0.1 M H₂SO₄, Feed flow rate: 400 cm³ min⁻¹,
Pseudo-emulsion flow rate: 200 cm³ min⁻¹.

Table 4 Comparison of the performance for the selective separation of SO₂ in SILMs^a (Ref 120)

ILS	Water content (mass fraction) ^b	Support	Experimental Condition	SO ₂ permeability (barrers)	SO ₂ /N ₂ selectivity	SO ₂ /CH ₄ selectivity	SO ₂ /CO ₂ selectivity
[N ₂₂₂₄][dimalonate]	762 ppm	Hydrophilic PES	Saturated humidified gas 0.05 bar, 40 ^o C	7208	585	271	18
[emim][CF ₃ SO ₃]	-	Hydrophilic PES	Saturated humidified gas 0.05 bar, 25 ^o C	13143	279	199	9.6
[emim][CF ₃ SO ₃] + GPA ^c	-	Hydrophilic PES	Saturated humidified gas 0.05 bar, 25 ^o C	9774	134	241	8.6

Abbreviations: [emim][CF₃SO₃]-1-ethyl-3-methylimidazolium trifluoromethanesulfone, GPA-glucose pentaacetate

The water content values are for neat ILS before permeation experiment

Table 5 Different approaches of mass transport modeling using HF contactors

Sl No	Application	Liquid membrane technology	Diffusive mass transport modeling approach	Mathematical philosophy
			Diffusion - Kinematic approach Overall mass transfer resistances are the summation of the resistances at feed phase membrane, strip phase. $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s}$	Mixed - kinematic approach Mathematical equation formulated based on surface renewal theory, and mass balance.
1	Cu (ii) E: LIX984N S: H ₂ SO ₄	HFRLM		
2	Cu (ii) & Co (ii) E: LIX984N & CYANEX 272	HFSLM	Mass transfer resistance is controlled by diffusion across feed phase, membrane and shell side $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s}$	Mass transfer equation of Cu (ii) and Co (ii) is based on surface renewal phenomenon and mass balance law considering d
3	Cs (I) E: Calix-[4]-bis (2,3-naphtho) – crown-6 S: Distilled Water	HFSLM	Cs (I) transfer resistance is the sum of resistance from aqueous phase and membrane phase. $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m}$	A simple mathematical model by using Fick's First law of diffusion at steady state condition. Model equation is derived by balancing solution concentration at feed reservoir and neglecting strip phase resistance.
4	Sr (II) E: DTBCH18C6 (Di-tert-dicyclohexane-18-crown-6) S: Distilled water	HFSLM	Mass transfer resistance is considered in the feed and membrane phase neglecting strip phase resistance. $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m}$	Mathematical model developed for prediction of strontium separation by using the Fick's first law of diffusion. Mass balance of the feed reservoir considering resistances of aqueous and organic phase gives the time variation of solution concentration equation.

5	Pb (ii)	HFSLM		Mathematical modeling : carried out with the rigorous approach by conserving mass in the hollow fiber membrane considering convection, reaction and accumulation of mass transfer flux in the hollow fiber membrane.
	E:D2EHPA (di-2-ethylhexyl phosphoric acid) S: HCl /H ₂ SO ₄ / HNO ₃			
6	(S) – amlodipine	HFSLM	Mass Transfer resistance is composed of feed phase resistance, membrane phase resistance and the strip phase resistance. Overall permeability resistance: $\frac{1}{P} = \frac{1}{K_f} + \frac{d_i}{d_{lm}} \frac{1}{DK_m} + \frac{d_i}{d_o} \frac{1}{K_s}$ $K_f = 2.74 \times 10^{-4} \text{ m/s}$ $K_m = 2.52 \times 10^{-4} \text{ m/s}$	
	E: Chiral selector O,O'- Dibenzoyl-(2S,3S)-tartaric acid((+)-DBTA) S: Benzenesulfonic acid			
7	Nd (iii)	HFSLM	The overall mass transfer resistance is the combine resistance of resistances at feed, membrane and strip phases. $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s}$ $D_m = 6 \times 10^{-12} \text{ m}^2/\text{s}$ $D_{hm} = 1.2 \times 10^{-10} \text{ m}^2/\text{s}$ K_{ex} is measured experimentally at desired condition	A simplified steady state mathematical model, where mass balance for both acid phases and membrane incorporated in the model equation to study the effect of acidity and sodium ion. To solve the model equations, the exit solution concentration is calculated from the hollow fiber characteristics and hydrodynamics
	E:TODGA S:HNO ₃			
8	Levocetirizine	HFSLM	Permeability resistance is sum of resistances at feed phase, membrane phase and the strip phase. $\frac{1}{P} = \frac{1}{K_f} + \frac{d_i}{d_{lm}} \frac{1}{DK_m} + \frac{d_i}{d_o} \frac{1}{K_s}$ $1/K_f = 4.150 \times 10^{-3} \text{ s/cm}$ $1/K_m = 5.291 \times 10^{-3} \text{ s/cm}$	Mathematical model : predicting the concentration of levocetirizine at extraction side of the liquid membrane considering overall mass transfer coefficient at each phase and the distribution ratio.
	E:O,O',-dibenzoyl-(2R,3R) -tartaric acid((-)-DBTA)			

9	Nd (iii) E: HEHEPA S:HNO ₃	HFSLM		Mathematical modeling : done with the rigorous approach with the conservation of mass at a segment of the hollow fibre membrane, which consists of convection, diffusion reaction and accumulation terms
10	Nd (iii) E:TODGA S: HNO ₃	HFSLM	The overall mass transfer resistance is the sum of resistances at feed, membrane and strip phases. $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s}$ $D_m = 6 \times 10^{-12} \text{ m}^2/\text{s}$ $D_{hm} = 1.2 \times 10^{-10} \text{ m}^2/\text{s}$	A mathematical equation derived by incorporating mass balance for both acid phases and TODGA. To solve the model equations, the exit solute concentration is calculated from the hollow fibre characteristics and hydrodynamics
11	Nd(iii) E: PC88A S: H ₂ SO ₄	HFSLM		Mass transfer resistance predominated by the resistance from extraction reaction and shell side as well. Overall resistance: $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_e} + \frac{1}{K_m} + \frac{1}{K_s}$ Where, $1/K_e = 5.871 \times 10^2 \text{ s/cm}$ $1/K_s = 1.896 \times 10^2 \text{ s/cm}$ $1/K_f = 0.966 \times 10^2 \text{ s/cm}$ $1/K_m = 0.285 \times 10^2 \text{ s/cm}$
12	Hg(ii) E : Aliquate 336 S : Thiourea	HFSLM		Time variation of solute concentration in feed reservoir depends mainly from the extraction reaction resistance. Overall resistance: $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_e} + \frac{1}{K_m} + \frac{1}{K_s}$ Where, $1/K_e = 5.182 \times 10^2 \text{ s/cm}$

				$1/K_s = 0.841 \times 10^2 \text{ s/cm}$ $1/K_f = 0.742 \times 10^2 \text{ s/cm}$ $1/K_m = 0.521 \times 10^2 \text{ s/cm}$	
13	Hg(ii) E : Aliquate 336 S : Thiourea	HFSLM			A rigorous mathematical model is developed by conserving mass with convection, diffusion, kinetic and accumulation of the Hg(ii) flux across the module.
14	U (vi) E: DNPPA S:H ₂ SO ₄	SLM	<p>Mass transfer resistance is the addition of aqueous phase and organic phase resistances.</p> $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m}$ <p>$1/K_f = 975.64 \pm 374.34 \text{ s/cm}$ $1/K_m = 69046.4 \pm 6757 \text{ s/cm}$</p>		Kinetic model is evaluated to calculate the mass transfer coefficients and diffusion coefficient for recovery of Uranium.
15	Cr (iii) E: RNH ₃ ⁺ HSO ₄ ⁻ S: H ₂ SO ₄	PEHFLM	<p>Permeation of Cr (iii) is the aqueous diffusion control.</p> $1/K = 5.263 \times 10^4 \text{ s/cm}$		Permeation model considers the linear concentration gradient and mass balances of the module and the respective reservoirs.
16	Phenol E: I-Decanol S: NaOH	PEHFLM	<p>The kinetics of phenol transfer from 1-decanol to NaOH is very slow compare to loading in to 1-decanol. The emulsion with NaOH rich adds advantage in the extraction process.</p> <p>The total resistance considered is</p> $\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m}$ <p>$1/K = 1.69 \times 10^{-6} \text{ s/m} - 0.546 \times 10^{-6} \text{ s/m}$</p>		A mathematical equation is formulated by mass balance across the feed reservoir and with consideration of diffusivity in mass transfer.
17	ZN (ii) E: CYANEX 272 S: H ₂ SO ₄	PEHFLM	<p>Mass transfer resistances are the summation of resistance at feed phase stagnant layer, membrane phase stagnant layer, membrane phase, strip boundary layer and extraction and back-extraction</p>		Model equations are generated by balancing mass at stirred tank and across the module with the diffusive mass transport

			reactions at interfaces.	
			$\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_e} + \frac{1}{K_m^o} + \frac{1}{K_m} + \frac{1}{K_{be}} + \frac{1}{K_s}$	
18	CO ₂ E:Distilled Water	NDSX	Steady state flux balance of gas phase to liquid phase considering the effect wetting behavior and the magnitude of the wetting. Overall resistance:	flux.
			$1/K = 3.33 \times 10^6 \text{ s/m} - 2.02 \times 10^6 \text{ s/m}$	
			$\frac{1}{Kd_{in}} = \frac{1}{K_f d_i} + \frac{1}{K_m d_{in}} + \frac{1}{HK_m^* d_{in}} + \frac{1}{HK_G d_o}$	Mathematical model : derived by balancing flux across the membrane with the consideration of the pore size distribution and the pressure drop across different wetting ratios.
19	CO ₂ E:MEA (Monoethanolamine)	NDSX	Overall mass transfer resistances are the summation of the resistances at liquid phase, wetted membrane phase, non wetted membrane phase and gas phase.	Mathematical equation : generated by balancing mass across the module with the linear variation of solute concentration.
			$\frac{1}{Kd_{in}} = \frac{1}{eK_i d_i} + \frac{1}{eK_M d_{in}^i} + \frac{1}{HK_M^* d_{in}} + \frac{1}{HK_G d_o}$	
20	Nd (iii) E:DNPPA & TOPO	NDSX	Mass transfer resistance of aqueous and organic phase films is considered as the resistances of the mass transfer	Model equation : formulated to get the time variation of feed concentration by mass balance at feed reservoir and across a single hollow fiber under no accumulation condition.
			$\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m}$	
21	Thiols' E:[C ₂ .mim][CF ₃ SO ₃]	NDSX	Although the extraction of thiol is the controlling step of the extraction process because of its low distribution ratio, overall mass transfer resistance is considered as the summation of the individual resistances at feed phase, ionic liquid boundary and at ionic liquid phase For Extraction:	Mass transfer flux : modeled by mass balance at module and feed reservoir. Regeneration of ionic liquid with sweet gas is integrated in the process and modeled with the material balance to the ionic liquid.
			$\frac{1}{K} = \frac{d_i}{d_o} \frac{1}{K_f} + \frac{d_i}{d_{im}} \frac{1}{K_m^i} + \frac{1}{DK_m}$	
			For Regeneration	

$$\frac{1}{K_{rg}} = \frac{d_i}{d_o} \frac{1}{K_g H} + \frac{d_i}{d_{lm}} \frac{1}{K_{mg}^i H} + \frac{1}{DK_{mr}}$$

$$1/K = 2.048 \pm 0.671 \times 10^7 \text{ s/m}$$

$$1/K_{rg} = 9.434 \pm 5 \times 10^7 \text{ s/m}$$

22 Ethanol or Acetone HFSCSX

E: Super critical solvent (near Critical CO₂)

23 Cu (ii) HFSCSX

E: CO₂ Phase containing TFA (1,1,1-trifluoro-2,4-pentaneodine) or HFA(1,1,1,5,5,5-hexafluoro-2,4-pentaneodine)

The total resistance is in-series approach mainly resulting from stagnant layers at inside and outside of the tube

$$\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_s}$$

Extraction modeling of ethanol or acetone is a rigorous approach, where the conservation of mass across the membrane with the diffusion in axial as well as in radial directions. The mass transfer model is by correlating effective rate functions for complex formation at the aqueous CO₂ interface based on molecular diffusion