



Review Paper

Review on Mechanism of Facilitated Transport on Liquid Membranes

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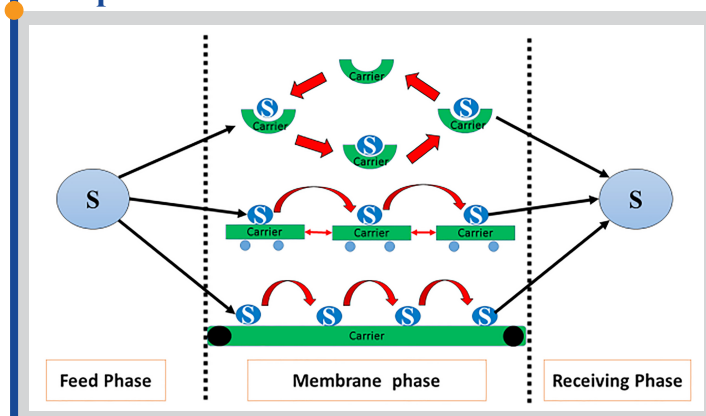
Keywords

Facilitated transport
Liquid membrane
Classifications
Membrane preparation

Highlights

- Principle and classification criteria of membranes
- Different type of liquid membranes
- Mechanism of facilitated transport on liquid membranes

Graphical abstract



Abstract

Membrane processes are used in various fields such as the environment, agriculture and different industrial sectors. These clean techniques are often adopted for directed processes such as treatment, recovery, valorization and separation. In this review article, the theoretical principles and the different classifications of liquid membranes, such as supported liquid membranes are discussed. Afterward, the mechanism of facilitated transport, and finally advantages and disadvantages of this technology are discussed, comprehensively.

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1. Introduction

Membrane processes are adopted as an ecological alternative, to purify, separate, recover or eliminate organic or inorganic substances from liquid or gas mediums, with minimal energy consumption, significantly reducing the volume of waste and without addition of toxic compounds. It is possible to extract the substances which are breakable or sensitive to temperature. In addition, the membrane technology is modular and able to work continuously. These processes are applicable in several economic sectors, such as the environment, energy, health, water treatment, cosmetic, food, and chemicals. The global market for membranes increasingly occupies an important place, and exceeded a figure of several billion dollars in 2015 and its growth is very regular, i.e., more than 10% per year.

According to the definition of "European Membrane House": a membrane is a permeable barrier, or semi-permeable, separating the two phases, which blocks or limits the movement of certain compounds. The phases on both sides of the membrane may be either in liquid phase or gaseous phase.

A liquid membrane is a liquid or supported liquid barrier which separates two phases (source phase and receptor phase), the chemical species can move through the membrane from the region with a high concentration to the region of low concentration of the same substrate. In this article, different types of membranes, their advantages and disadvantages, and the process of transportation and extraction of some invaluable compounds are reviewed.

2. Classification of membrane processes

The term 'membrane processes', is used to designate a set of tools implementing a semi-permeable membrane for separation and recovery or removal of species contained in a mixture. The various membrane processes are distinguished by:

- The chemical nature of the membrane
- The structure of the membrane
- The implementation and operation mode
- The type of force (or force gradient) used
- The nature of the phases in contact with the membrane
- The size, nature of the substrates to be treated

2.1. Chemical nature of membrane

The chemical nature of the membrane is one of the most important criteria of preparation. In fact, membranes can be developed from polymer materials, ceramics, metals, glass or combination of two or more of these. The choice of matching the specifications and physicochemical properties of materials is then crucial. The membrane must have good inertia against chemical agents, temperature variations and mechanical stresses of use. The materials used for the preparation of membranes include three major categories of membranes: organic, inorganic and composites membranes like supported liquid membranes (SLM).

2.2. Membrane structures

The structure of the membrane is an important factor, it governs the

transport mechanism and extraction. The organic, inorganic or composite membranes, can be classified into two categories using a porosity as a criteria.

2.2.1. Dense membranes

Dense membranes are considered as a homogenous material where thickness varies between 1 and 300 μm , depending on the mechanical performance of the material. The permeability decreases inversely with the thickness. For these types of membranes, the fraction of amorphous and crystalline area of the material strongly influences the performance of extraction of species, and consequently their selectivity, the result of a phenomenon of diffusion-dissolution where the polymer-solvent interactions and polymer-substrate are crucial. These non-porous membranes mainly are used in the gas treatment area (gas permeation, and pervaporation) or reverse osmosis.

2.2.2. Porous membranes

Porous membranes are heterogeneous materials that are used in the processes of liquid-liquid or solid-liquid filtration. The sizes of the pores can rank as recommended by the *International Union of Pure Chemistry*, and on the definition of porosity in solids, into three categories:

- Microporous for a pore diameter less than 2 nm.
- Mesoporous for a pore diameter between 2 and 50 nm
- Macroporous for a pore diameter greater than 50 nm.

according to the morphology of the two types of membranes (dense and porous), can be divided into two other categories:

2.2.3. Symmetric membranes

Symmetric membranes are isotropic materials. This defines a material which has only one compound. For porous materials, the symmetrical term specifies that the diameters of all the pores are comparable throughout the thickness.

2.2.4. Asymmetric membranes

Asymmetric membranes are anisotropic materials. They are represented by combinations of materials (composite membrane) or by a pore size variation of the same material in the thickness

2.3. Modules

By definition, a module is a basic set of a separation installation or extraction membranes comprising one or more filter elements (membranes), frames, separators, plates or inserts drains, pipes and joints needed for fluid flow [1]. There are several types of modules that correspond to the different geometries adopted for the membranes. For selecting a module and therefore a membrane geometry, many factors should be taken into account. Among them, we can mention the congestion (the ratio between the area of membrane and the volume of module configuration), the fouling that is inherent to operating mode and hydrodynamic flows, membrane cleaning, cost of investment and operation, and lifetime of membranes. The main advantages and disadvantages of the four major commercial types of modules are summarized in [Table 1](#).

Table 1
The main advantages and disadvantages of different modules.

Module	Advantages	Disadvantages
Flat sheet	- Low energy consumption - Easy cleaning - Fouling low	- High investment - High Dimensions - Pretreatment - Low Filter area
Tubular	- Simple technology - Average Cleaning - Fouling medium - Simplified Pretreatment	- High investment - High energy consumption - High Dimensions
Spiral	- Fouling medium - Low space requirement - Low investment - Average Energy consumption	- Pretreatment - Cleaning hard
Capillary	- Low energy consumption - Very small dimensions	- High Fouling - Difficult cleaning - High investment - Replacement of membranes is expensive

2.4. Driving force

Generally, any process requires an energy input to achieve the transfer operation of the material from one phase to the other. This contribution results in a difference in chemical or physical potential that is represented by the driving force of the process. The processes can be classified according to the type of employed driving force for material transfer to operate an extraction or separation process. Major driving forces used in membrane processes

include *i*) the gradient of the concentration (ΔC), *ii*) the electrical potential gradient ($\Delta\phi$), *iii*) the temperature gradient (ΔT); and *iv*) the pressure gradient (ΔP) [2].

3. Classification of liquid membranes

There are several types of membranes used in the liquid phase, like bulk liquid membranes (BLM), emulsion liquid membrane (ELM), supported liquid membrane (SLM), and supported ionic liquid membrane (SILM).

3.1. Bulk liquid membrane (BLM)

Bulk Liquid Membrane is more particularly designed to implement experiments in laboratory scale, to test a new processes or improving existing systems, so it is a fundamental tool for studying phenomena of facilitated extraction or transport. The organic membrane phase comprising a carrier, dissolved in an organic solvent that is placed in the bottom of the tube (see Figure 1). This membrane phase separates other aqueous phases, source and receiver.

The experimental device or bridge Schulmann (see Figure 1-a) consists of a U-shaped tube where the three phases are placed in contact. This system provides stable hydrodynamic conditions. Burgard et al [3] have modified this system by using a rotary cylinder (see Figure 1-b). In this type of membrane, the volume of the membrane phase is most important with respect to the volumes of source and receiving phases, which requires a large quantity of the carrier.

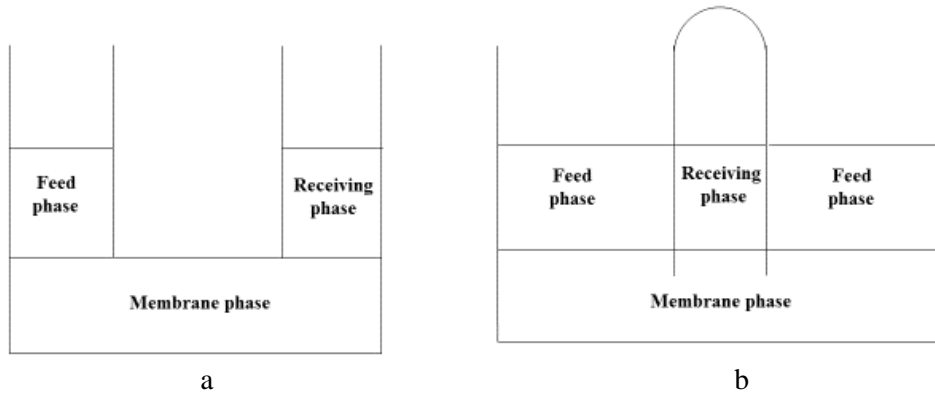


Fig. 1. Bulk liquid membrane: a) U-tube (bridge Schulmann) and b) cell with a rotating bell [3].

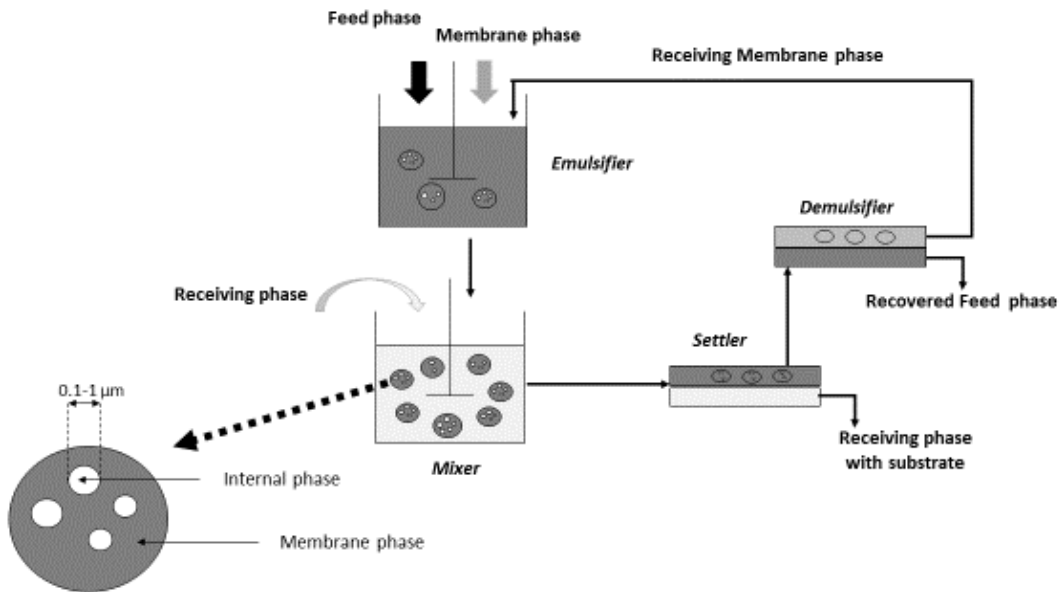


Fig. 2. The different steps relating to processes of ELM (adopted from) [4].

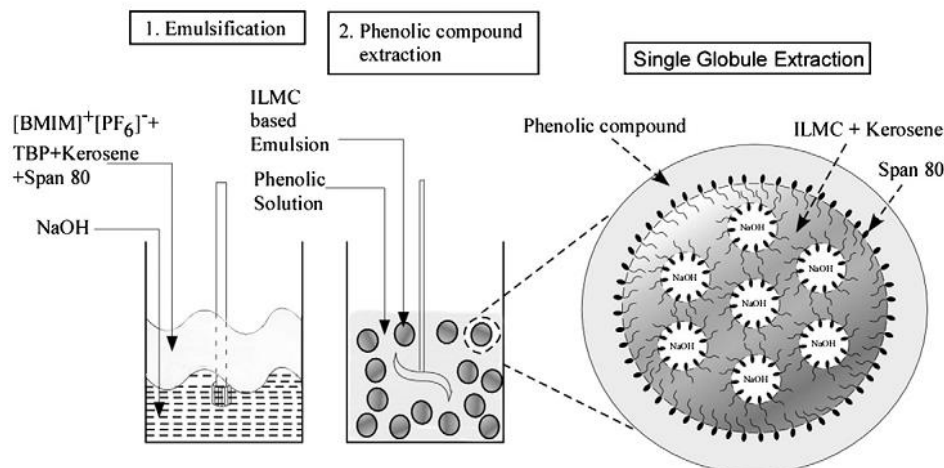


Fig. 3. Elimination of phenolic compounds using an ion mixing in ELM [5].

BLM are used to study the selectivity and kinetic transport parameters of amino acids using the D2EHPA as a carrier, that dissolved in kerosene [6]. Chakrabarty et al. [7] conducted a comprehensive study to extract *Lignosulfonate* (LS) from the waste with Trioctyleamin (TOA) as the carrier. The transport of metal ions is also studied by this type of membrane such as uranium [8,9], palladium [10], vanadium [11], copper [12,13], chromium [14], and cadmium [15,16]. Recently, new configuration of BLM have been developed which includes for example: bulk hybrid liquid membrane (BHLM) [17], and bulk ionic liquid membrane (BILM) [18].

3.2. Emulsion liquid membrane (ELM)

In 1968, the ELM was used to separate the hydrocarbons [19]. This type of membrane consists of three phases (see Figure 2): an external, a membrane, and an internal phases. The external phase or the source phase contains the substrate to be extracted; the membrane phase separates physically the external and internal phases. Moreover, it contains a surfactant to stabilize the emulsion. In the internal or the receiving phase, the substrate migrates in one way of the external phase through the membrane into internal phase, where this substrate converted to another species. The driving force of this diffusion is a difference in concentration of the substrate between the external and internal phases. Figure 2 shows the four stages of this membrane process:

ELM is used to recover organic compounds. For example, Chanukya et al. [20] have used hexane and heptane solvents such as membrane phases and Span 80 as a surfactant to extract alcohol from diluted solutions, several factors are studied such as speed and time of stirring, also the concentration of the carrier. In another study, Balasubramanian et al. [5] have conducted an experimental study about the elimination of phenolic compounds from aqueous solutions using the mixed ionic liquid carrier (MILC) containing 1-Butyl 3 Methylimidazolium Hexafluorophosphate $[BMIM]^+[PF_6]^-$, dissolved in Tributyl phosphate (TBP) (see Figure 3). The various factors are examined such as, concentrations of TBP, the concentration of surfactant, emulsification time, the volume ratio of the phases, the stirring rate, the pH of the external phase and the concentration of the mixture $[BMIM + PF_6]$ in the TBP for remove of phenol. For example, the addition of 0.02% (v/v) $[BMIM + PF_6]$ in the membrane phase improved the emulsion stability by a factor of 5 times.

ELM can also be used to extract metal ions. García et al. [21] arrived to extract 94% of Cr (III) ions in 5 min of experience and the membrane ELM is stable up to 30 minutes with the PC-88A as a carrier (see Figure 4). Ahmad et al. [22] investigated the extraction of Cd (II) ions with TOA as the carrier. Many other studies carried out to extract the metal ions such as uranium [23], chromium [24], copper [25], arsenic [26], as well as other metals [4].

The major problem of this type of liquid membranes (ELM) is the difficulty of controlling the stability of the emulsion. However, it has to control multiple parameters simultaneously, such as ionic strength, pH, the stirring speed, and stirring time.

3.3. Supported liquid membranes (SLM)

3.3.1. Design

The supported liquid membrane (SLM) or the immobilized liquid

membranes (ILM) are the liquid impregnated or immobilized in a porous material used as support. This support can be an inert microporous polymer, chemically stable, like the polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE), where the support is impregnated with an organic solvent (immiscible with water), containing a complexing agent (hydrophobic amphiphilic) (carrier) of substrates. The supported liquid membranes exhibit high selectivity to compounds extracting, by the interaction of the substrate with the carrier and the formation of (carrier-substrate) entity. The carrier is considered as a catalyst so that it can be used several times because it is recycled and reused with a small quantity [27].

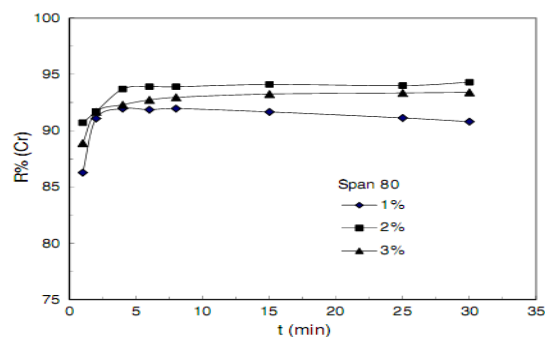


Fig. 4. Effect of the concentration of the carrier on the stability of ELM [21].

The objective of using a module is to hold the wet porous polymer in the liquid phase to increase the mechanical stability of the system, ensure a large effective surface area and a free circulation of the load between the feed phase and receiving phase. Several configurations of SLM membranes, can meet these requirements. They are determined by the shape of the applied module (see Figure 5). The most popular are "Hollow-fiber Supported Liquid Membrane (HFSLM)" (Figure 5-A), "Flat-Sheet Supported Liquid Membrane (FL-SLM)" (Figure 5-B), and there is also the spiral form (Figure 5-C).

The configuration of the hollow fibers has been used in industrial applications. For instance, Rosell et al. [28] studied the effect of the "design" of this configuration on the extraction of vanadium by Aliquat 336 as carrier agent. Indeed, the membrane surface increases with the number of fibers used, but the flux decreases because of the steric hindrance effect between the fibers. Di Lucio et al. [29] demonstrated that, this configuration provides high selectivity for extraction of the compound fructose present in mixtures of sugars, using boric acid as an extractive agent. On contrary, the flat sheet configuration of SLM is often used at laboratory scale because it is simple and flexible. The transport process in SLM is a combination of two simultaneous steps, including extraction and reextraction. The first one is sharing the substrate between the aqueous source and the organic membrane phases by interaction of substrate with the free carrier in membrane (formation of substrate-carrier), and the second step is sharing the substrate between the membrane and the receiving phases by dissociation of the entity

form [30]. On the other hand, it should be noted that the technique of supported liquid membranes is used for the extraction of organic compounds [31–37] and also the metal ions [38–55].

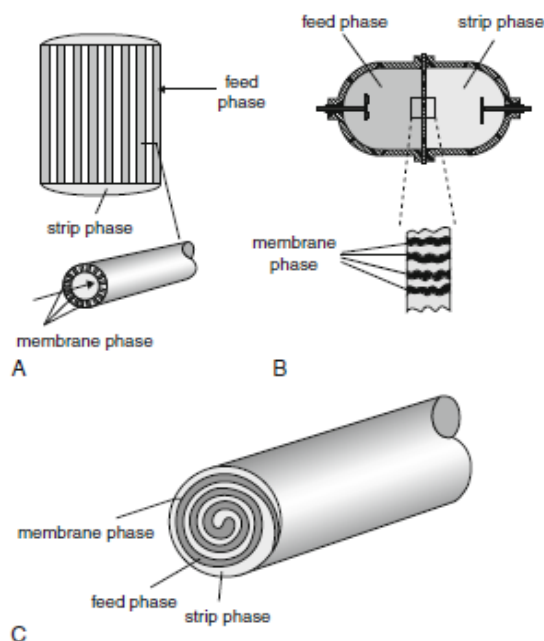


Fig. 5. Different configurations of supported liquid membrane: (A) HF-SLM, (B) FS-SLM and (C) spiral (adopted from [30]).

3.3.2. Components of SLM

Generally, SLM consists of three essential components: a polymeric support, a carrier which is often an amphiphilic supramolecule, and an organic solvent (see Figure 6). The physicochemical properties of these three components have a very important key role on the performance of the SLM and performance of the phenomenon of extraction and facilitated transport.

3.3.2.1. Support

The support is made of a hydrophobic polymer that has high strength and is chemically inert. For making membrane supports either as flat or other form, mostly the polypropylene (PP), Polyvinylidene fluoride PVDF, Polytetrafluoroethylene PTFE or polyether sulfone (PES), Celgard® 2500 are used [56–59]. In order to have the highest possible transport flows by membrane surface unit, the supports must be very porous, in other words their porosity which is the ratio of the pore volume to the total volume must be as large as possible. The porosities between 45 and 75% are available from porous polymeric membrane suppliers.

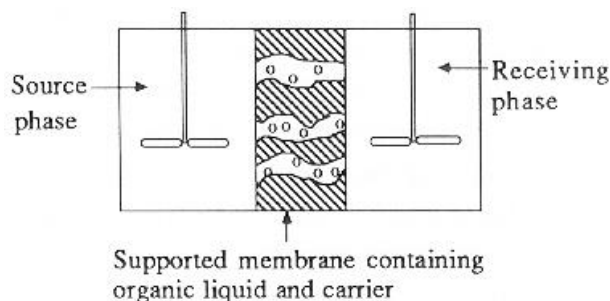


Fig. 6. The various constituents of SLM.

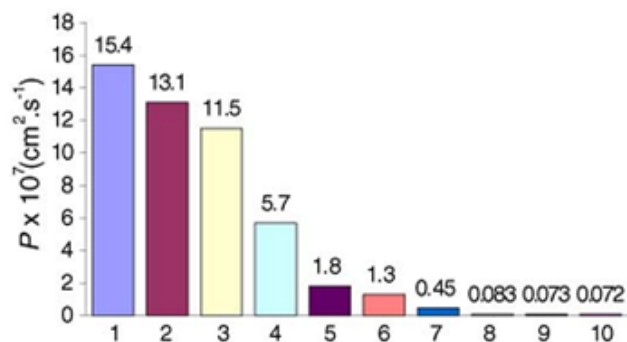


Fig. 7. Influence of the nature of the solvent on the facilitated extraction of glucose by SLMs: Permeabilities for 0.05 glucose of SLMs impregnated with different solvents: (1) Benzene; (2) Toluene; (3) Xylene; (4) Ethylbenzene; (5) Cumene; (6) Mesitylene (1,3,5-trimethylbenzene); (7) Tert-butylbenzene; (8) 2-Chlorotoluene; (9) Decalin (cis, trans-decahydronaphthalene); (10) Heptane, the solvent used was the commercial mixture of three xylene isomers and ethylbenzene [33].

3.3.2.2. Extractive agent

The extractive agent or carrier is an amphiphilic molecule that ensures and promotes the transport of a substrate from the source phase to the receiving phase, other authors use the term complexing agent or ligand to describe the association between the molecule carrier and the substrate to be transported or extracting. This molecule should be strongly hydrophobic in order to minimize its loss by dissolution in the extra membrane phases, and stay trapped in the membrane phase. However, this agent must have a hydrophilic part as a site for binding to the substrate.

The most conventional carriers are antibiotics, carboxylic acids, phosphoric, sulfonic acids, amines, crown ethers or to extract the metal ions or organic compounds ions [34,60–62]. There is also a new family of carriers are ionic liquids where the carrier is in the form of an organic mixture of an ion pair or a single charged molecule, these carriers have an advantages over the classical carriers, especially to extract charged compounds such as metal ions [63–65].

3.3.2.3. Organic phase (Solvent)

The solvent should be immiscible with the aqueous phases, which its solubility should be as low as possible. It must also have a low vapor pressure to avoid evaporation during the extraction process. The most used solvents are kerosene, dodecane, toluene, and xylene [33,66–68]. To study the influence by the nature of the organic phase (solvent) on the facilitated transport Hassoun et al. [33] have studied the influence of the solvent on the facilitated transport of sugars by an SLM containing methyl cholate as a carrier agent (see Figure 7).

3.3.3. Experimental setup

The cell used to perform the experiments of facilitated transport is composed of two compartments (source phase *F* and receiving phase *R*), separated by the membrane (*M*). The system is immersed in a thermostatic bath (*TB*) containing water. The homogeneity is ensured by a multi-stirrer (*MS*) (see Figure 8).

SLM membrane is prepared by impregnation of microporous support in a solution containing a known mass of the carrier dissolved in a given volume of organic solvent for several hours (Figure 9) [69].

3.3.3. Factors affecting the efficiency and stability of SLM

3.3.3.1. The factors affecting the stability of SLM

The stability of SLM is affected by several factors including the nature of the support [70,71], solvent [33], carrier agent, extract of the substrate and also the physical-chemical composition of the source and receiving phases (pH, substrate concentration, and co-ions in nature), and other important factors, i.e., stirring speed and temperature of environment [72,73].

It should be noted that the stability of the entity (substrate-carrier) should be moderate, to ensure transportation of this entity from (source-membrane) interface, to (membrane- receiving) interface, because, it must to ensure the dissociation of this entity at the second interface. More stable entity may cause a complete fouling where the extraction of the substrate is practically zero.

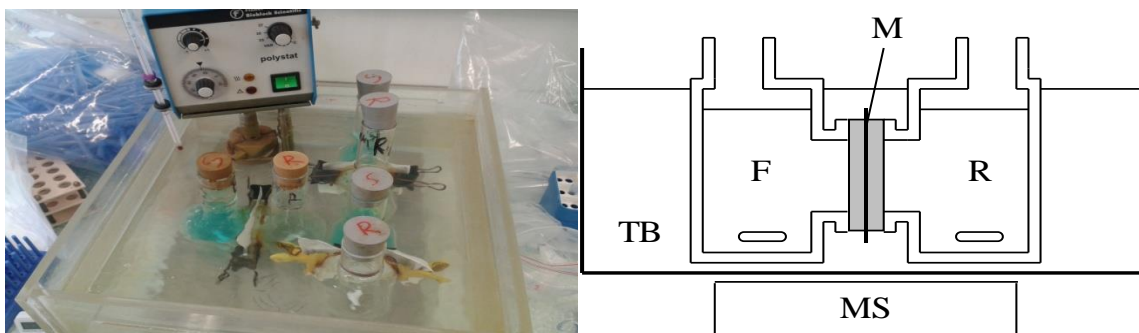


Fig. 8. Representation of the experimental device used. (the original picture from our lab and the scheme is from [34]).

3.3.3.2. Some approaches to overcome the instability of SLM

The supported liquid membranes present many advantages at laboratory scale, which make them a good candidate for some large industrial applications. However, the instability problem of membrane phase with the time affects lifetime of this membrane type. As this problem is caused by the gradual loss of membrane phase in both aqueous solutions (source and receiving), through the formation of emulsions at the two interfaces of the membrane. This failure also causes contamination of two aqueous phases and can also destroy the separation unit, completely [74]. Researchers from the University of Twente (The Netherlands) indicate that the stability of an SLM is maintained when there is no loss of membrane phase and the flow of material through the membrane remains constant [75]. Consequently, re-impregnation of the support with the membrane phase is not a good solution when the loss is significant. Zhang et al. measured the loss of membrane phase in the case of several supports (PVDF, cellulose acetate, etc.) impregnated in n-decanol as the organic phase [76].

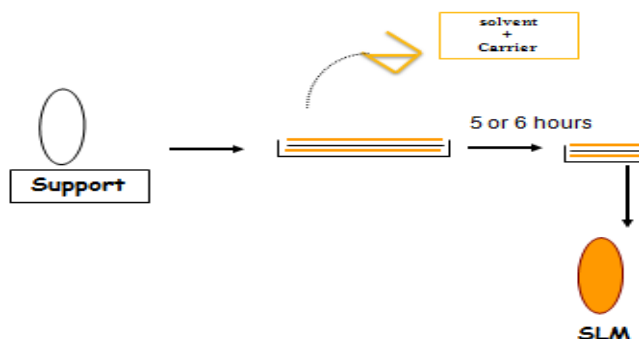


Fig. 9. The preparation of SLM membrane.

Other researchers consider a SLM is stable if the flux remains constant, even if there is a loss of the membrane phase. Van Voode et al. have studied the stability of SLM with Celgard as support, a mixture of two carriers LIX 860-I and Cyanex 302 in kerosene as the solvent to extract the Nickel (II) with a constant flux during 650 h [77]. To overcome the problems of the instability of supported liquid membranes, several approaches have been developed, such as:

1. The support (polymer, pores, thickness, etc.) and the constituents of the organic phase (solvent and carrier agent) must be selected carefully in order to minimize the tendency of the membrane phase out the pores [78,79].
2. The re-impregnation of membrane supports with the organic phase, in the study by Yang et al. [80], the flow of copper was recovered to the initial value after re-impregnation of the membrane used after about 40 h. However, for a long-term operation, the flow of copper decreased further with time even if the membrane was re-impregnated with a fresh organic solution (see Figure 10). SEM images indicate that the morphology of the membrane was changed after using it continuously for 600 hours. It clearly appears that the pore size becomes larger and the pore structure are changed (the pores become dilated and more elliptical). The large pore sizes are well known for poor stability of SLM. Therefore, for a long-term operation, membrane structural changes are potentially important factors that affect the life and stability of the SLM.

3. The most common way in recent years to overcome this handicap instability SLM and to have more effective membranes is thinking about fixing or trap the carrier agent in the support matrix, hence the birth of membranes such as polymer inclusion membrane for (PIM), or grafted polymer membranes (GPM).

3.4. Polymer inclusion membrane (PIM)

Polymer inclusion membranes (PIM), plasticized polymer membrane (PPM) or fixed site membrane (FSM) are produced by the evaporation of a volatile solvent containing a matrix polymer such as cellulose triacetate (CTA) or polyvinyl chloride (PVC), a plasticizer, and a carrier [81]. They are used to extract small organic molecules and metal ions [82], orthophosphates [83], cadmium [84], chromium [45,85], and cerium [86]. Kolev et al. have elaborated a membrane with PVC and di(2-ethylhexyl) phosphoric acid (D2EHPA) agent, and they developed a mathematical model for the process of extraction and recovery facilitated the uranium ions [87].

Several studies are conducted on the stability of this type of membranes, e.g., Kagayaa et al. [88] have studied the influence of salts and acids on the stability of a membrane with PVC as a polymeric support and Aliquat 336 as carrier. Scindia et al. [89] have demonstrated that polymer inclusion membrane with CTA as a support and Aliquat 336 as a carrier, is stable for 30 days, compare to a supported liquid membrane which is not even stable for 7 days. Authors have got to develop a new type of membrane (the pore-filled membrane (PFM)) which can be stable over 3 months. The polymer inclusion membrane has low permeabilities relative to other membranes despite their significant stabilities.

3.5. Grafted polymer membranes (GPM)

The grafted polymer membranes (GPM) or functionalized polymer membranes (FPM) are porous ultrafiltration and microfiltration membranes modified by introducing of chemical groups into the basic structure to make them physically and chemically stable to improve its selectivity and efficiency. The porous structure of the membrane acts as a support for the stabilization of the grafted molecules that may be brittle. So, a more stable composite material, for example, hydrogels are widely used in the pharmaceutical field [90,91]. However, they are unable to withstand mechanical forces, hence the idea to immobilize it in the matrix of porous membranes to increase their mechanical stability without affecting their transport process for use in industrial applications [92,93]. In order to form dense or porous polymers membranes, that can realize this operation, either by *in situ* polymerization or by grafting large or small chain molecules on polymeric matrix. In both cases, the addition of these molecules in the membrane matrix can change the various properties of the membrane such as permeability, flux, mechanical resistance, efficiency, biocompatibility, reactivity and conductivity environment and capacity of the transport and extraction.

In general, polymers can be functionalized in any matrix where the porous structure provides sufficient interaction between the polymer and the structure to be grafted. The organic polymers used in the manufacture of this type of membranes include the fluoro-polymers [94–97], cellulosic material [98–100], polysulfides [101–103], polycarbonates [104,105] and polyacrylates [106]. These polymers are widely used for the preparation of the grafted membranes because they are relatively stable.

The development of membrane materials containers immobilized biomolecules or grafted as polyacids, proteins, and enzymes enables the development of high performance materials and high selectivity. Therefore, the grafting of molecules in the polymer matrix improves the properties of the membranes as the acid-base character, the catalytic properties, so these types

of functionalized membranes can be used for the extraction and separation of ions metal, organic molecules, or decontamination and detoxification of contaminated environments.

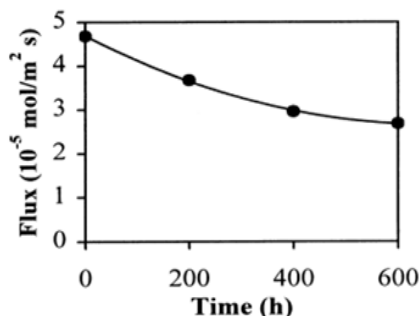


Fig. 10. Improving the stability of a membrane by technique of reimpregnation: Long term permeation with reimpregnated membrane. Each data point was taken after impregnation with ML supported liquid membrane, 10% (v/v) LIX 984N-Kerosene-Celgard 2500; the copper flux was measured at standad conditions: feed, 2 g/l Cu²⁺, pH 2.5; strip, 2M H₂SO₄ containing 2g/l Cu²⁺; stirring speed, 450 rpm [80].

The preparation of these smart materials, by the grafting technique via two essential ways either by the creation of a covalent or non-covalent binding, generally, the modification is to use *in situ* polymerization technique [107,108], or the grafting technique of the molecules on a polymer support [109,110].

4. Mechanisms of facilitated transport

4.1. The different types of processes related to membrane transport

In analogy to biological membranes, the transfer phenomenon of a substance through the membrane phase can be achieved either by passive transport or active transport (or directed).

4.1.1. Passive transport

Simple diffusion or passive transport occurs involving only the physical properties of the membrane. The system is governed by the sharing of the substrate between the aqueous phase and the membrane phase and by their diffusion through the membrane under the effect of the concentration gradient (see Figure 11-a).

4.1.2. Facilitated transport

In active transport or facilitated (also directed), membrane phase contains

a carrier dissolved in an organic solvent the transfer of the substrate through the membrane phase is done according to the model of the double layers [111] by the following steps:

- 1- Diffusion of the substrate (S) in the stagnant layer of the source phase.
- 2- The association between the carrier (C) and the substrate at the first interface between the source and the membrane phase.
- 3- Diffusion of the entity (carrier-substrate (C-S)) in the membrane phase to the 2nd membrane interface.
- 4- Dissociation of the entity and regeneration of carrier.
- 5- Diffusion of the substrate in the receiving phase.

The carrier acts as a catalyst because it increases the solubility of the chemical space in the membrane by promoting the transfer speed. The transfer of the material process stops when the concentration gradient between the feed phase and receiving is zero.

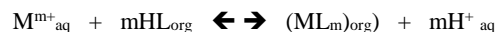
If there is only one specie being transported, we talk about simple facilitated transport (see Figure 11-b) and, if the source phase contains two species, that are able to associate with the carrier, we are talking about coupled facilitated transport and there are two possibilities:

- *Co-transport*: This type of transport or extraction is observed when the carrier is neutral in nature, and the feed phase contains a pair of ions (M^{m+} mX⁻) (cation and anion) associated and extracted (dissociated) reversibly by carrier L (Figure 12), and each of the two interfaces can be observed in one of the reactions of the following equilibrium:



The cation and anion migrate in the same direction of the source phase to the receiving phase, under the double combined effect, the concentration gradient, especially by their association with the carrier.

- *Counter Transport*: In this case, the carrier can be acidic or basic nature, it's possible to find counter transport of anions or cations. For counter cation transport, the carrier in the membrane phase is an acid, and this process is done by a cation-exchange proton (pH pump), cations migrate in the opposite direction protons (high pH to low pH) (Figure 13), in this case, the balance in the source-membrane interface is written as:



The process counter facilitated transport of anions can take place when the carrier in the membrane phase can exchange an anion (basic agent) by interaction with the substrate at source phase-membrane interface, in this case there is formation of neutral entity (A⁻L⁺) on the balance:

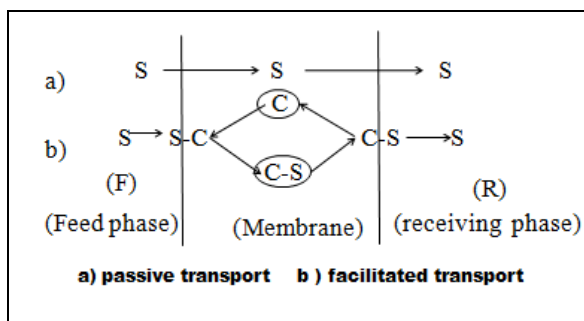


Fig. 11. Principle of the transfer of material through the membranes.

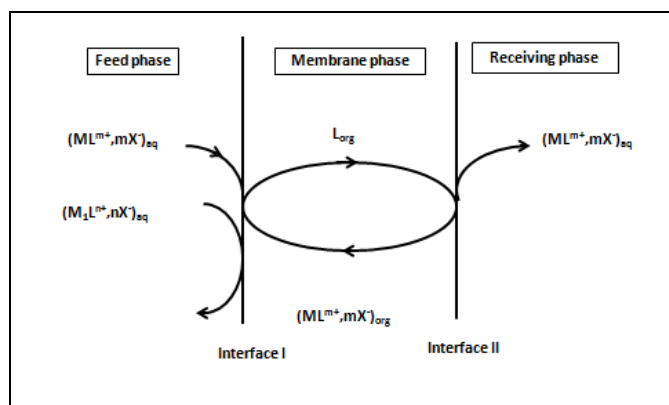


Fig. 12. Principle of co-facilitated transport (Adopted from [30]).

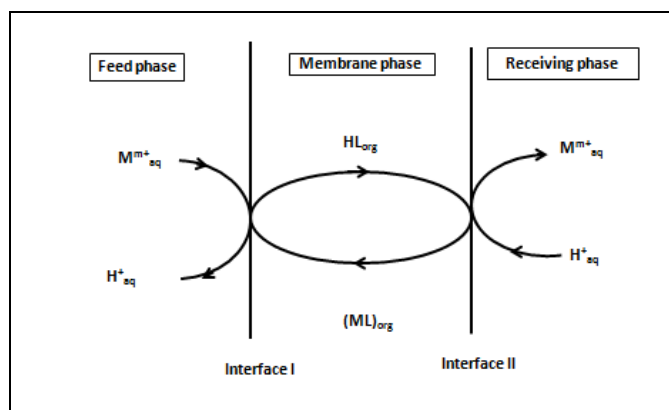
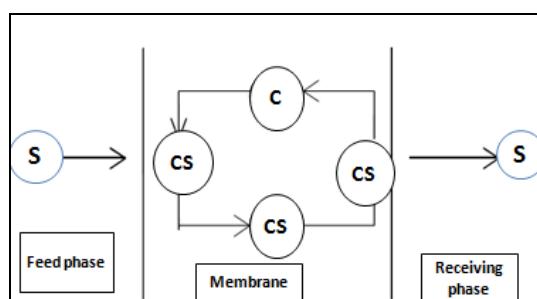
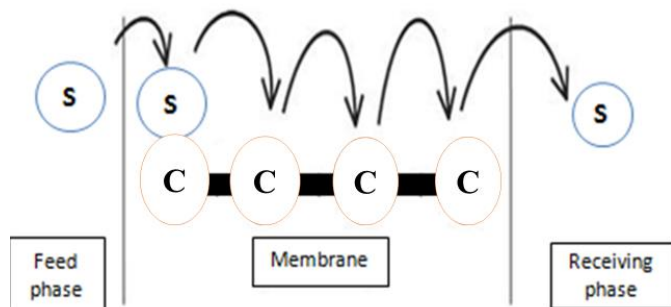


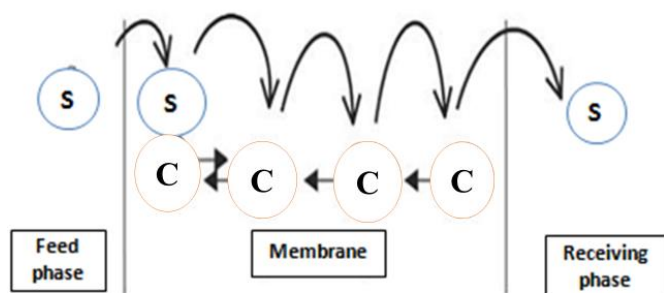
Fig. 13. Principle counter facilitated transport (pH pump) (adopted from [30]).



(a) Solution-diffusion mechanism (pure diffusion).



(b) Mechanism by jumping on fixed sites.



(c) Mechanism by jumping on mobile sites.

Fig. 14. Different mechanisms proposed for the facilitated transport process [112].

The neutral entity $(A \cdot L^+)$ diffused in the membrane phase and at receiving phase-membrane interface, the anion A^- is released and diffuses into the receiving phase but the cationic species L^+ associates with another anion X^- present in the receiving phase to form LX that diffuses through the membrane phase in the opposite direction of A^- so that X^- diffuses into the source phase.

In this case, the process is governed by association between the substrate and carrier, the gradient of the concentration of anion X^- and electro neutrality of the source and receiving phases.

4.2. Different facilitated transport mechanisms

To exploit the transport process and the extraction existing and future design of system more selective and more efficient, we have to find models to explain these phenomena of material transfer through the membranes. Several models have been proposed to elucidate the process of facilitated transport, according to the work performed by Smith and Hassoun [34,113]. There are three different mechanisms:

* A solution-diffusion mechanism (Figure 14-a): the carrier is movable in the membrane phase; the migration of (substrate-carrier) and the carrier is in the opposite direction of membrane phase. This type of mechanism is favorable in the case of liquid membranes as SLM and BLM.

* One mechanism by jumping on fixed sites (Figure 14-b): the substrate moves successively by binding to several carriers fixed sites that are considered sites of interaction, this type of mechanism is common in solid membranes such as PIM and GPM.

* A mechanism by jumping on mobile sites (Figure 14-c): the substrate moves by the successive migration on several mobile carrier sites, this model is suitable for SLM to explain the higher values of the diffusion coefficients through these types of membranes.

5. Conclusions

This paper summarizes the different classification of membranes using several criteria's like the chemistry, physique nature or geometry of membrane. There are the symmetric, asymmetric, dense and porous membranes. After this, the paper focuses on liquid membranes because they present many advantages like high selectivity and technical feasibility as both laboratory and industrial scales. bulk liquid membrane (BLM) and emulsion liquid membrane (ELM), and supported liquid membrane (SLM), this last one is used more and more because the thickness is very low then others liquid membranes, so, the flux and selectivity are very high, and the quantity of chemical is low. After this, the manuscript presents the preparation method, and discusses the several factors affecting the stability performance of SLM. Finally, the different type of processes and mechanisms of facilitated transport (solution-diffusion, jumping on the fixed or mobile sites) are discussed in detail. In addition, some solutions are presented to increase the stability of supported liquid membrane.

References

- [1] S. Chevalier, Modélisation mathématique des mécanismes de séparation en nanofiltration, Thesis, University of Bordeaux I, 1999.
- [2] N. Lakshminarayanaiah, Transport phenomena in membranes, Acad. Press. 1969.
- [3] M. Burgard, L. Jurdy, H.S. Park, R. Heimburger, Liquid-liquid extraction and liquid membranes: an analysis of transport rates of potassium and rubidium salts through a liquid membrane containing dibenzo 18 crown 6, Nouv. J. Chim. 7 (1983) 575-578.
- [4] M. Ma, B. Chen, X. Luo, H. Tan, D. He, Q. Xie, S. Yao, Study on the transport selectivity and kinetics of amino acids through di(2-ethylhexyl) phosphoric acid-kerosene bulk liquid membrane, J. Membr. Sci. 234 (2004) 101-109.
- [5] K. Chakrabarty, K.V. Krishna, P. Saha, A.K. Ghoshal, Extraction and recovery of

- lignosulfonate from its aqueous solution using bulk liquid membrane, *J. Membr. Sci.* 330 (2009) 135–144.
- [6] M. Shamsipur, R. Davarkhah, A.R. Khanchi, Facilitated transport of uranium(VI) across a bulk liquid membrane containing thenoyltrifluoroacetone in the presence of crown ethers as synergistic agents, *Sep. Purif. Technol.* 71 (2010) 63–69.
- [7] A.M. Candela, V. Benatti, C. Palet, Pre-concentration of Uranium (VI) using bulk liquid and supported liquid membrane systems optimized containing bis(2-ethylhexyl) phosphoric acid as carrier in low concentrations, *Sep. Purif. Technol.* 120 (2013) 172–179.
- [8] I. Akin, S. Erdemir, M. Yilmaz, M. Ersoz, Calix[4]arene derivative bearing imidazole groups as carrier for the transport of palladium by using bulk liquid membrane, *J. Hazard. Mater.* 223 (2012) 24–30.
- [9] J.J. Pinto, M. García-Vargas, C. Moreno, A bulk liquid membrane–flow injection (BLM–FI) coupled system for the preconcentration and determination of vanadium in saline waters, *Talanta* 103 (2013) 161–165.
- [10] S.H. Chang, T.T. Teng, I. Norli, Cu(II) transport through soybean oil-based bulk liquid membrane: Kinetic study, *Chem. Eng. J.* 173 (2011) 352–360.
- [11] T.R. Reddy, J. Ramkumar, S. Chandramouleeswaran, A.V.R. Reddy, Selective transport of copper across a bulk liquid membrane using 8-hydroxy quinoline as carrier, *J. Membr. Sci.* 351 (2010) 11–15.
- [12] S. Alpaydin, A.Ö. Saf, S. Bozkurt, A. Sirit, Kinetic study on removal of toxic metal Cr(VI) through a bulk liquid membrane containing p-tert-butylcalix[4]arene derivative, *Desalination* 275 (2011) 166–171.
- [13] S. Koter, P. Szczepański, M. Mateescu, G. Nechifor, L. Badalau, I. Koter, Modeling of the cadmium transport through a bulk liquid membrane, *Sep. Purif. Technol.* 107 (2013) 135–143.
- [14] D. He, M. Ma, Z. Zhao, Transport of cadmium ions through a liquid membrane containing amine extractants as carriers, *J. Membr. Sci.* 169 (2000) 53–59.
- [15] T.Z. Sadyrbaeva, Hybrid liquid membrane – Electrolysis process for extraction of manganese(II), *Desalination* 274 (2011) 220–225.
- [16] M. Chakraborty, H.-J. Bart, Highly selective and efficient transport of toluene in bulk ionic liquid membranes containing Ag⁺ as carrier, *Fuel Process. Technol.* 88 (2007) 43–49.
- [17] N.L. Norman, separating hydrocarbons with liquid membranes, *United States Pat. Off.* 3 410 794 (1968).
- [18] B.S. Chanukya, N.K. Rastogi, Extraction of alcohol from wine and color extracts using liquid emulsion membrane, *Sep. Purif. Technol.* 105 (2013) 41–47.
- [19] A. Balasubramanian, S. Venkatesan, Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid [BMM]+[PF6]⁻ in Tributyl phosphate, *Desalination* 289 (2012) 27–34.
- [20] M.G. García, A.O. Acosta, J. Marchese, Emulsion liquid membrane pertraction of Cr(III) from aqueous solutions using PC-88A as carrier, *Desalination* 318 (2013) 88–96.
- [21] A.F. Ismail, M. Khayet, A.L. Ahmad, A. Kusumastuti, C.J.C. Derek, B.S. Ooi, Emulsion liquid membrane for cadmium removal: Studies on emulsion diameter and stability, *Desalination* 287 (2012) 30–34.
- [22] P.S. Kulkarni, S. Mukhopadhyay, M.P. Bellary, S.K. Ghosh, Studies on membrane stability and recovery of uranium (VI) from aqueous solutions using a liquid emulsion membrane process, *Hydrometallurgy* 64 (2002) 49–58.
- [23] A. Bhowal, G. Bhattacharyya, B. Inturu, S. Datta, Continuous removal of hexavalent chromium by emulsion liquid membrane in a modified spray column, *Sep. Purif. Technol.* 99 (2012) 69–76.
- [24] H. ZHENG, J. CHEN, B. WANG, S. ZHAO, Recovery of Copper Ions from Wastewater by Hollow Fiber Supported Emulsion Liquid Membrane, *Chinese J. Chem. Eng.* 21 (2013) 827–834.
- [25] S. Kiani, S.M. Mousavi, Ultrasound assisted preparation of water in oil emulsions and their application in arsenic (V) removal from water in an emulsion liquid membrane process, *Ultrasound. Sonochem.* 20 (2013) 373–377.
- [26] J.H. Meldon, A.L. Ahmad, A. Kusumastuti, C.J.C. Derek, B.S. Ooi, Emulsion liquid membrane for heavy metal removal: An overview on emulsion stabilization and destabilization, *Chem. Eng. J.* 171 (2011) 870–882.
- [27] O. Loiacono, E. Drioli, R. Molinari, Metal ion separation and concentration with supported liquid membranes, *J. Membr. Sci.* 28 (1986) 123–138.
- [28] A. Rosell, C. Palet, M. Valiente, Selective separation and concentration of vanadium(V) by a chemical pumping hollow-fiber supported liquid membrane, *Anal. Chim. Acta.* 349 (1997) 171–178.
- [29] M. Di Luccio, B.D. Smith, T. Kida, T.L.M. Alves, C.P. Borges, Evaluation of flat sheet and hollow fiber supported liquid membranes for fructose pertraction from a mixture of sugars, *Desalination* 148 (2002) 213–220.
- [30] V. S., Kislik, *Liquid membrane principles and application in chemical separations and wastewater treatment*, 2010th ed., Elsevier, Amsterdam, 2010.
- [31] E. Miyako, T. Maruyama, N. Kamiya, M. Goto, Transport of organic acids through a supported liquid membrane driven by lipase-catalyzed reactions., *J. Biosci. Bioeng.* 96 (2003) 370–374.
- [32] N. Tbeur, T. Rhlalou, M. Hlaibi, D. Langevin, M. Métayer, J.F. Verchère, Molecular recognition of carbohydrates by a resorcinarene. Selective transport of alditols through a supported liquid membrane., *Carbohydr. Res.* 329 (2000) 409–422.
- [33] H. Hassoune, T. Rhlalou, M.J.F.V. Michel, M. Métayer, J.-F. Verchère, Facilitated transport of aldoses by methyl cholate through supported liquid membranes impregnated with various solvents, *J. Membr. Sci.* 248 (2005) 89–98.
- [34] H. Hassoune, T. Rhlalou, J.-F. Verchère, Mechanism of transport of sugars across a supported liquid membrane using methyl cholate as mobile carrier, *Desalination* 242 (2009) 84–95.
- [35] G.O. Yahaya, B.J. Brisdon, R. England, Facilitated transport of lactic acid and its ethyl ester by supported liquid membranes containing functionalized polyorganosiloxanes as carriers, *J. Membr. Sci.* 168 (2000) 187–201.
- [36] K. Chakraborty, P. Saha, A.K. Ghoshal, Simultaneous separation of mercury and lignosulfonate from aqueous solution using supported liquid membrane, *J. Membr. Sci.* 346 (2010) 395–401.
- [37] M. Hlaibi, N. Tbeur, A. Benjjar, O. Kamal, L. Lebrun, Carbohydrate - resorcinarene complexes involved in the facilitated transport of alditols across a supported liquid membrane, *J. Membr. Sci.* 377 (2011) 231–240.
- [38] L. Soko, E. Cukrowska, L. Chimuka, Extraction and preconcentration of Cr (VI) from urine using supported liquid membrane, *Anal. Chim. Acta.* 474 (2002) 59–68.
- [39] P. Ura, R. Prakorn, P. Weerawat, H. Milan, Feasibility Study on the Separation of Uranium and Thorium by a Hollow Fiber Supported Liquid Membrane and Mass Transfer Modeling, *J. Ind Eng. Chem.* 12 (2006) 673–681.
- [40] L. PEI, B. YAO, X. Fu, Study on transport of Dy(III) by dispersion supported liquid membrane, *J. Rare Earths.* 27 (2009) 447–456.
- [41] C. Palet, M. Mufioz, M. Hidalgo, M. Valiente, Transport of vanadium (V) through a triacetyltrimethylammonium solid supported liquid membrane from aqueous acetic acid / acetate solutions, *J. Membr. Sci.* 98 (1995) 241–248.
- [42] S. Shailesh, P.N. Pathak, P.K. Mohapatra, V.K. Manchanda, Transport studies of uranium across a supported liquid membrane containing N,N-di(2-ethylhexyl) isobutyramide (D2EHIBA) as the carrier, *J. Membr. Sci.* 272 (2006) 143–151.
- [43] H.J. Cristau, D. Virieux, J.F. Dozol, H. Rouquette, Selective extraction of actinides by polyphosphine polyoxides through supported liquid membrane, *J. Radioanal. Nucl. Chem.* 241 (1999) 543–547.
- [44] K. Ochrowicz, W. Apostoluk, Modelling of carrier mediated transport of chromium(III) in the supported liquid membrane system with D2EHPA, *Sep. Purif. Technol.* 72 (2010) 112–117.
- [45] A. Benjjar, T. Eljaddi, O. Kamal, K. Touaj, L. Lebrun, M. Hlaibi, The development of new supported liquid membranes (SLMs) with agents: Methyl cholate and resorcinarene as carriers for the removal of dichromate ions (Cr₂O₇²⁻), *J. Environ. Chem. Eng.* 2 (2014) 503–509.
- [46] P.K. Parhi, N.N. Das, K. Sarangi, Extraction of cadmium from dilute solution using supported liquid membrane, *J. Hazard. Mater.* 172 (2009) 773–779.
- [47] O.N. Ata, Modelling of copper ion transport through supported liquid membrane containing LIX 984, *Hydrometallurgy* 77 (2005) 269–277.
- [48] S. a. Ansari, P.K. Mohapatra, D.R. Prabhu, V.K. Manchanda, Transport of lanthanides and fission products through supported liquid membranes containing N,N,N',N'-tetraoctyl diglycolamide (TODGA) as the carrier, *Desalination* 232 (2008) 254–261.
- [49] F. Valenzuela, C. Basualto, A. Acosta, Transport of molybdenum with Alamine 336 using supported liquid membrane, *Hydrometallurgy* 72 (2004) 309–317.
- [50] C. Kozłowski, W. Walkowiak, Applicability of liquid membranes in chromium(VI) transport with amines as ion carriers, *J. Membr. Sci.* 266 (2005) 143–150.
- [51] K. Chakraborty, P. Saha, A.K. Ghoshal, Separation of mercury from its aqueous solution through supported liquid membrane using environmentally benign diluent, *J. Membr. Sci.* 350 (2010) 395–401.
- [52] C. Fontas, R. Tayeb, S. Tingry, M. Hidalgo, P. Seta, Transport of platinum(IV) through supported liquid membrane (SLM) and polymeric plasticized membrane (PPM), *J. Membr. Sci.* 263 (2005) 96–102.
- [53] O. Arous, Comparison of carrier-facilitated silver (i) and copper (ii) ions transport mechanisms in a supported liquid membrane and in a plasticized cellulose triacetate membrane, *J. Membr. Sci.* 241 (2004) 177–185.
- [54] L. Pei, B. Yao, C. Zhang, Transport of Tm(III) through dispersion supported liquid membrane containing PC-88A in kerosene as the carrier, *Sep. Purif. Technol.* 65 (2009) 220–227.
- [55] S. Suren, T. Wongsawa, U. Pancharoen, T. Prapasawat, A.W. Lothongkum, Uphill transport and mathematical model of Pb(II) from dilute synthetic lead-containing solutions across hollow fiber supported liquid membrane, *Chem. Eng. J.* 191 (2012) 503–511.
- [56] G. Muthuraman, K. Palanivelu, Transport of textile dye in vegetable oils based supported liquid membrane, *Dye. Pigment.* 70 (2006) 99–104.
- [57] P. Kubáň, P. Boček, Direct coupling of supported liquid membranes to capillary electrophoresis for analysis of complex samples: A tutorial, *Anal. Chim. Acta.* 787 (2013) 10–23.
- [58] P. Kazemi, M. Peydayesh, A. Bandegi, T. Mohammadi, O. Bakhtiari, Stability and extraction study of phenolic wastewater treatment by supported liquid membrane using tributyl phosphate and sesame oil as liquid membrane, *Chem. Eng. Res. Des.* 1324 (2013) 1–9.
- [59] I.B. Solangi, F. Özcan, G. Arslan, M. Ersöz, Transportation of Cr(VI) through calix[4]arene based supported liquid membrane, *Sep. Purif. Technol.* 118 (2013) 470–478.
- [60] I. Ortiz Uribe, M. Fallanza, A. Ortiz, D. Gorri, I. Ortiz, Experimental study of the separation of propane/propylene mixtures by supported ionic liquid membranes containing Ag⁺-RTILs as carrier, *Sep. Purif. Technol.* 97 (2012) 83–89.
- [61] V.K. Manchanda, P.K. Mohapatra, D.R. Raut, S.A. Ansari, A. Sarkar, Selective transport of radio-caesium by supported liquid membranes containing calix[4]crown-6 ligands as the mobile carrier, *Desalination* 232 (2008) 262–271.
- [62] S. Azzoug, O. Arous, H. Kerdjoudj, Metallic ions extraction and transport in supported liquid membrane using organo-phosphoric compounds as mobile carriers, *J. Environ. Chem. Eng.* 2 (2014) 154–162.
- [63] M.A. Malik, M.A. Hashim, F. Nabi, Ionic liquids in supported liquid membrane technology, *Chem. Eng. J.* 171 (2011) 242–254.
- [64] S. Nosrati, N.S. Jayakumar, M.A. Hashim, S. Mukhopadhyay, Performance evaluation of vanadium (IV) transport through supported ionic liquid membrane, *J. Taiwan Inst. Chem. Eng.* 44 (2013) 337–342.
- [65] M.T. Coll, A. Fortuny, A.M. Sastre, Boron reduction by supported liquid membranes using ALiCY and ALiDEC ionic liquids as carriers, *Chem. Eng. Res. Des.* 30 (2013) 758–763.
- [66] S. Panja, P.K.K. Mohapatra, S.C.C. Tripathi, V.K.K. Manchanda, Facilitated transport of uranium(VI) across supported liquid membranes containing T2EHDGA as the carrier extractant, *J. Hazard. Mater.* 188 (2011) 281–287.

- [67] M.H.H. Mahmoud, C.P. Huang, H.A. Elliott, M.H.H. Mahmoud, Effective separation of iron from titanium by transport through TOA supported liquid membrane, *Sep. Purif. Technol.* 84 (2012) 63–71.
- [68] B. Swain, J. Jeong, J. Lee, G.-H. Lee, Extraction of Co(II) by supported liquid membrane and solvent extraction using Cyanex 272 as an extractant: A comparison study, *J. Membr. Sci.* 288 (2007) 139–148.
- [69] A. Benjar, M. Hor, M. Riri, T. Eljaddi, O. Kamal, L. Lebrun, A new supported liquid membrane (SLM) with methyl cholate for facilitated transport of dichromate ions from mineral acids: parameters and mechanism relating to the transport, *J. Mater. Environ. Sci.* 3 (2012) 826–839.
- [70] C. Zidi, R. Tayeb, M. Dhahbi, Extraction of phenol from aqueous solutions by means of supported liquid membrane (MLS) containing tri-n-octyl phosphine oxide (TOPO), *J. Hazard. Mater.* 194 (2011) 62–68.
- [71] J.J. Close, K. Farmer, S.S. Moganty, R.E. Baltus, CO₂/N₂ separations using nanoporous alumina-supported ionic liquid membranes: Effect of the support on separation performance, *J. Membr. Sci.* 390 (2012) 201–210.
- [72] S. Biswas, P.N. Pathak, S.B. Roy, Carrier facilitated transport of uranium across supported liquid membrane using dinonyl phenyl phosphoric acid and its mixture with neutral donors, *Desalination* 290 (2012) 74–82.
- [73] A. Surucu, V. Eyupoglu, O. Tutkun, Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier, *J. Ind. Eng. Chem.* 18 (2012) 629–634.
- [74] R. Chiarizia, Stability of supported liquid membranes containing longchain aliphatic amines as carriers, *J. Membr. Sci.* 55 (1991) 65–77.
- [75] A. Kemperman, D. Bargeman, T. van den Boomgaard, H. Strathmann, The stability of supported liquid membranes: A state of the art literature review, *Sep. Sci. Technol.* 31 (1996) 2733–2762.
- [76] B. Zhang, G. Gozzelino, G. Baldi, Membrane liquid loss of supported liquid membrane based on n-decanol, *Colloids Surfaces A Physicochem. Eng. Asp.* 193 (2001) 61–70.
- [77] I. Van de Voorde, L. Pinoy, R.F. De Ketelaere, Recovery of nickel ions by supported liquid membrane (SLM) extraction, *J. Membr. Sci.* 234 (2004) 11–21.
- [78] P. Deblay, S. Delepine, M. Minier, H. Renon, Selection of Organic Phases for Optimal Stability and Efficiency of Flat-Sheet Supported Liquid Membranes, *Sep. Sci. Technol.* 26 (1991) 97–116.
- [79] T. Shinbo, T. Yamaguchi, H. Yanagishita, K. Sakaki, D. Kitamoto, M. Sugiura, Supported liquid membranes for enantioselective transport of amino acid mediated by chiral crown ether - effect of membrane solvent on transport rate and membrane stability, *J. Membr. Sci.* 84 (1993) 241–248.
- [80] X.J. Yang, A.G. Fane, Performance and stability of supported liquid membranes using LIX 984N for copper transport, *J. Membr. Sci.* 156 (1999) 251–263.
- [81] C. Fontàs, R. Tayeb, M. Dhahbi, E. Gaudichet, F. Thominette, P. Roy, K. Steenkeste, M.-P. Fontaine-Aupart, S. Tingry, E. Tronel-Peyroz, Polymer inclusion membranes: The concept of fixed sites membrane revised, *J. Membr. Sci.* 290 (2007) 62–72.
- [82] 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), *J. Membr. Sci.* 281 (2006) 7–41.
- [83] D.P. Francis, D.I. McKelvie, P.A. Shalliker, D.P. Nesterenko, D.M. Macka, E.A. Nagul, C. Fontàs, I.D. McKelvie, R.W. Cattrall, S.D. Kolev, The use of a polymer inclusion membrane for separation and preconcentration of orthophosphate in flow analysis, *Anal. Chim. Acta.* 803 (2013) 82–90.
- [84] O. Kebiche-Senhajji, L. Mansouri, S. Tingry, P. Seta, M. Benamor, Facilitated Cd(II) transport across CTA polymer inclusion membrane using anion (Aliquat 336) and cation (D2EHPA) metal carriers, *J. Membr. Sci.* 310 (2008) 438–445.
- [85] R.A. Kumbasar, Selective extraction of chromium (VI) from multicomponent acidic solutions by emulsion liquid membranes using tributylphosphate as carrier, *J. Hazard. Mater.* 178 (2010) 875–882.
- [86] K. Hiratani, S.P. Kusumochayho, N. Kameta, K. Sugaya, T. Shinbo, T. Kanamori, Synthesis of Noncyclic Carriers for Cerium Ion Transport through Polymer Inclusion Membrane, *Chem. Lett.* 34 (2005) 1636–1637.
- [87] 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, *J. Membr. Sci.* 409 (2012) 242–250.
- [88] S. Kagaya, Y. Ryokan, R.W. Cattrall, S.D. Kolev, Stability studies of poly(vinyl chloride)-based polymer inclusion membranes containing Aliquat 336 as a carrier, *Sep. Purif. Technol.* 101 (2012) 69–75.
- [89] Y.M. Scindia, A.K. Pandey, A.V.R. Reddy, Coupled-diffusion transport of Cr(VI) across anion-exchange membranes prepared by physical and chemical immobilization methods, *J. Membr. Sci.* 249 (2005) 143–152.
- [90] A.S. Hoffman, Hydrogels for biomedical applications, *Adv. Drug Deliv. Rev.* 54 (2002) 3–12.
- [91] N.A. Peppas, P. Bures, W. Leobandung, H. Ichikawa, Hydrogels in pharmaceutical formulations, *Eur. J. Pharm. Biopharm.* 50 (2000) 27–46.
- [92] V. Kapur, J.C. Charkoudian, S.B. Kessler, J.L. Anderson, Hydrodynamic permeability of hydrogels stabilized within porous membranes, *Ind. Eng. Chem. Res.* 35 (1996) 3179–3185.
- [93] M. Ulbricht, Advanced functional polymer membranes, *Polymer* 47 (2006) 2217–2262.
- [94] G.G. Kumar, A.R. Kim, K.S. Nahm, D.J. Yoo, R. Elizabeth, High ion and lower molecular transportation of the poly vinylidene fluoride-hexa fluoro propylene hybrid membranes for the high temperature and lower humidity direct methanol fuel cell applications, *J. Power Sources.* 195 (2010) 5922–5928.
- [95] M.T. Guzmán-Gutiérrez, M.H. Rios-Dominguez, F.A. Ruiz-Treviño, M.G. Zolotukhin, J. Balmaseda, D. Fritsch, E. Prokhorov, Structure-properties relationship for the gas transport properties of new fluoro-containing aromatic polymers, *J. Membr. Sci.* 385–386 (2011) 277–284.
- [96] G. Ellinghorst, J. Fuehrer, D. Vierkotten, Radiation initiated grafting on fluoro polymers for membrane preparation, *Radiat. Phys. Chem.* 18 (1981) 889–897.
- [97] H. Nomura, P.W. Kramer, H. Yasuda, Preparation of gas separation membranes by plasma polymerization with fluoro compounds, *Thin Solid Films.* 118 (1984) 187–195.
- [98] K. Ishihara, R. Takayama, N. Nakabayashi, K. Fukumoto, J. Aoki, Improvement of blood compatibility on cellulose dialysis membrane. Blood compatibility of phospholipid polymer grafted cellulose membrane, *Biomaterials* 13 (1992) 235–239.
- [99] M. Tu, W. Han, R. Zeng, S.M. Best, R.E. Cameron, A study of surface morphology and phase separation of polymer/cellulose liquid crystal composite membranes, *Colloid. Surf. A Physicochem. Eng. Asp.* 407 (2012) 126–132.
- [100] R. Barbucci, M. Casolaro, A. Magnani, The role of poly electrolytes in the permeability control of insulin: Behavior of poly(N-acryloyl-glycine) grafted on porous cellulose membrane, *J. Control. Release* 17 (1991) 79–88.
- [101] C. Shen, Q. Meng, G. Zhang, Chemical modification of polysulfone membrane by polyethylene glycol for resisting drug adsorption and self-assembly of hepatocytes, *J. Membr. Sci.* 369 (2011) 474–481.
- [102] R. Patel, S.J. Im, Y.T. Ko, J.H. Kim, B.R. Min, Preparation and characterization of proton conducting polysulfone grafted poly(styrene sulfonic acid) polyelectrolyte membranes, *J. Ind. Eng. Chem.* 15 (2009) 299–303.
- [103] H.J. Song, C.K. Kim, Fabrication and properties of ultrafiltration membranes composed of polysulfone and poly(1-vinylpyrrolidone) grafted silica nanoparticles, *J. Membr. Sci.* 444 (2013) 318–326.
- [104] R. Xie, L. Chu, W. Chen, W. Xiao, H. Wang, J. Qu, Characterization of microstructure of poly(isopropylacrylamide)-grafted polycarbonate track-etched membranes prepared by plasma-graft pore-filling polymerization, *J. Membr. Sci.* 258 (2005) 157–166.
- [105] S.J. Lue, C.-H. Chen, C.-M. Shih, M.-C. Tsai, C.-Y. Kuo, J.-Y. Lai, Grafting of poly(N-isopropylacrylamide-co-acrylic acid) on micro-porous polycarbonate films: Regulating lower critical solution temperatures for drug controlled release, *J. Membr. Sci.* 379 (2011) 330–340.
- [106] M. Ulbricht, G. Belfort, Surface modification of ultrafiltration membranes by low temperature plasma II. Graft polymerization onto polyacrylonitrile and polysulfone, *J. Membr. Sci.* 111 (1996) 193–215.
- [107] V. Kapur, J.C. Charkoudian, S.B. Kessler, J.L. Anderson, Hydrodynamic permeability of hydrogels stabilized within porous membranes, *Ind. Eng. Chem. Res.* 35 (1996) 3179–3185.
- [108] R. Childs, Nano-filtration using pore-filled membranes: effect of polyelectrolyte composition on performance, *Sep. Purif. Technol.* 22–23 (2001) 507–517.
- [109] Y. Ito, Signal-responsive gating by a polyelectrolyte pelage on a nanoporous membrane, *Nanotechnology* 9 (1998) 205–207.
- [110] A.M. Hollman, D. Bhattacharyya, Controlled Permeability and Ion Exclusion in Microporous Membranes Functionalized with Poly(1- γ -glutamic acid), *Langmuir* 18 (2002) 5946–5952.
- [111] W.K. Lewis, W.G. Whitman, Principles of Gas Absorption., *Ind. Eng. Chem.* 16 (1924) 1215–1220.
- [112] K.M. White, B.D. Smith, P.J. Duggan, S.L. Sheahan, E.M. Tyndall, Mechanism of facilitated saccharide transport through plasticized cellulose triacetate membranes, *J. Membr. Sci.* 194 (2001) 165–175.