

Recent advances in supported liquid membrane technology

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Abstract

Supported liquid membranes (SLM) are studied in various fields like analytical, inorganic and organic chemistry, chemical engineering, biotechnology and biomedical engineering. This technique offers the advantages of active transport, possible usage of expensive carriers, high selectivity, easy scale-up, low energy requirements, low capital and operating costs, etc. This paper gives a brief overview of mechanism and kinetic studies of SLM based separations. The problems with stability and possible applications of SLM are also reviewed.
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Keywords: Supported liquid membrane; Separation; Application

1. Overview

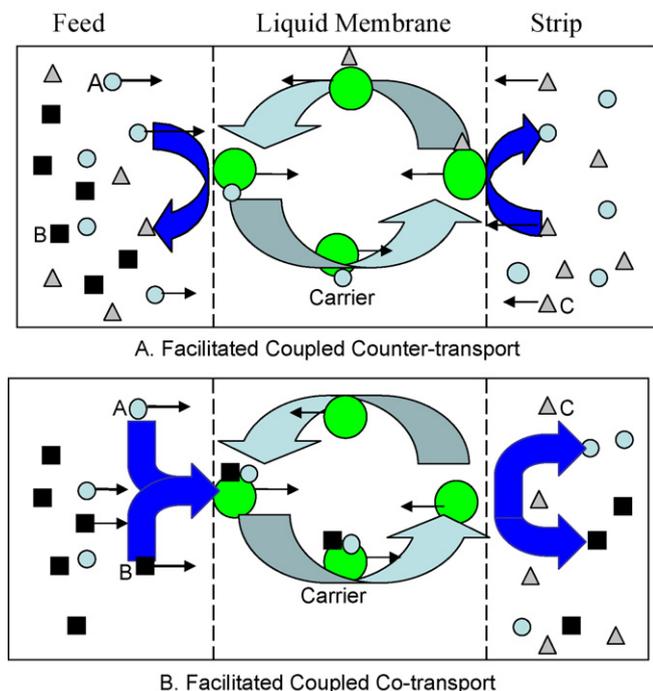
Membranes are not only more widely used in different new chemical engineering separation processes, they are also able to substitute existing separation and purification technologies. Well-known examples are pressure driven different types of filtration and reverse osmosis, electrical field driven electrodialysis and its new modification, continuous deionization, and finally gas and vapor separation processes where the driving factor often is a combination of pressure, concentration difference and also temperature. Using linear thermodynamics, it is possible to demonstrate that external pressure is much less efficient driving factor in the case of liquid/liquid separations on a molecular level. It is also well-known that transport through biomembranes is usually driven by concentration difference and transmembrane voltage.

If the process is based on diffusion, the membrane permeability for the transported species, which has to be as high as possible, is determined by the expression KD_m/L , and to increase permeability and selectivity one has to use chemical affinity (change distribution coefficient K), decrease membrane thickness L (biomembranes have the thickness of only two lipid molecules) and finally to increase diffusion coefficient in the membrane D_m . The idea to use thin organic liquid layer separating two aqueous phases seems very attractive from this point of

view simply because the D_m value in liquids is at least three–four orders of value higher than in solid polymer and inorganic membranes [1,2]. Besides that it is possible to dissolve some hydrophobic chemicals in the organic liquid, so that they will be able to interact with the transported hydrophilic species. This process would remind extraction, can be based on fine chemical interactions and can be highly specific. Then the complex could easily diffuse through the organic liquid. Though the value of D for the complex is slightly less than that for smaller species penetrating directly, the value of K can be increased by many orders of value, which results in so-called facilitated transport and much higher rates of process. Bloch was probably the first who has proposed to use extraction reagents dissolved in an organic solution and immobilized on microporous inert supports for removal of metal ions from a mixture [3].

Liquid membranes may be broadly classified into three types: bulk, emulsion and supported liquid membranes (SLM). Bulk liquid membranes usually consist of an aqueous feed and stripping phase, separated by a water-immiscible liquid membrane phase in a U-tube. BLMs are often used to study the transport properties of novel carriers and a small membrane surface area of BLMs makes them technologically not very attractive. Emulsion liquid membranes suggested by Li [4] have a very high surface area per unit of volume and low thickness and it means the separation process and accumulation inside the emulsion vehicle is fast. The problem is that the vehicles have to be produced before the process; they have to be stable enough so that leakage is reduced to minimum, but still not very stable so that they could be destroyed after the separation, thus allowing the

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Scheme 1. Facilitated coupled transport of ions through liquid membrane.

removal of the transported species. As the result the process has to use several unit operations and becomes technologically not very attractive.

In SLM, usually organic liquid is imbedded in small pores of a polymer support and is kept there by capillary forces. If the organic liquid is immiscible with the aqueous feed and strip streams, SLM can be used to separate the two aqueous phases. It may also contain an extractant, a diluent which is generally an inert organic solvent to adjust viscosity and sometimes also a modifier to avoid so-called third phase formation. Relatively small volume of organic components in the membrane and simultaneous extraction and reextraction in one technological step offers the advantages of possible usage of expensive carriers, high separation factors, easy scale-up, low energy requirements, low capital and operating costs, etc.

Scheme 1A shows the mechanism of SLM based separation of ions. In this case, charged species A from the feed solution are selectively extracted by the carrier through organic membrane/feed interface. The carrier picks up A, moves across the membrane as a complex and finally exchanges A with the charged species C on the other side of membrane. In this case, C has the same charge as A. To preserve electrical neutrality the carrier acts as a shuttle carrying A and C in the opposite directions. That is why the process is called facilitated coupled counter-transport. The most typical example of this process is metal cation exchange with H^+ ions, facilitated by acidic carriers. Basic carriers, like amines, can be used to carry H^+ ions together with negatively charged ions, such as Cl^- in the same direction. This process is called facilitated coupled co-transport (Scheme 1B).

It is easy to make the feed and strip solutions with different pH, so that ion exchange processes on the two membrane

surfaces will be shifted in opposite directions. This creates a concentration gradient of different forms of the carrier (with and without ions) in the membrane, and results in the directed ion flux through the membrane. Evidently the process leads to the transport of targeted ionic species across the membrane against their concentration gradient. This type of so-called “uphill” or active transport will continue until one driving factor (difference of chemical potentials of H^+ ions) is balanced by difference of chemical potentials of another transported ion. If the carrier selectively extracts A in the presence of B, A in the feed mixture will be finally separated from B, and then purified and concentrated in the strip solution. It is important that the process is using only chemical energy as a driving factor, and does not need transmembrane pressure or voltage.

Common configurations of SLM are flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM). Small experimental laboratory setup usually consists of a two-compartment cell, separated by a flat membrane. If the SLM is not stable and organic liquid does not stay in the pores, it is possible to use cells with three compartments where two porous supports of same [5] or different nature [6] are used to separate the organic and aqueous phases. The support in this case often is hydrophilic and is filled with aqueous solutions. The organic solution with the carrier can be stirred or circulated in the middle compartment to decrease mass transfer resistance.

Hollow fiber modules are usually more expensive but they offer much higher surface area per unit of module volume up to 500 m^{-1} . Commercially available modules can be big enough and have up to 220 m^2 area. In the case of HFSLM, there are several modes of operation [7]. In the simplest case the organic solvent with a carrier is filling the pores of the microporous walls of hollow tubes. Usually the feed solution is circulated through the lumen and the strip solution on the shell side of the hollow fibers to make the reextraction faster. To avoid the problems due to low stability of organic liquid phase in the pores, in another mode aqueous and organic solutions flow continuously with both phases coming into contact through the pores of the fiber wall. In such a case, only one unit operation, either extraction or back-extraction, is realized in one module and it is necessary to use two modules for the whole process. Pressure difference (higher in the non-wetting liquid) is applied to avoid phase entrainment. To carry out these two separation operations simultaneously, contained liquid membranes (CLM) can be used. In this case, the extracting organic solvent is contained in the interstices of two sets of microporous hollow fibers [8]. The feed solution passes through the lumen of one set. The strip solution flows in the lumen of the other set. Each aqueous–organic interface is immobilized at the respective fiber by applying the correct pressure difference. Modules with three sets of hollow fibers were introduced to conduct simultaneous separation of cations and anions using two different carriers and two different stripping solutions [9].

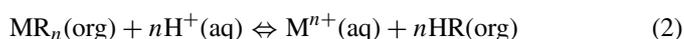
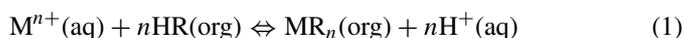
Usually SLMs are based on organic solvent separating two aqueous solutions, but in some cases the arrangements were opposite, and the pores in the polymer support separating two non-aqueous phases were impregnated by water [10]. The

problem with this arrangement is that water has relatively high volatility and the membrane is not stable. It seems that this problem can be solved using relatively new materials, so-called ionic liquids. In this case, a bulk organic cation, being apart from its anion is chemically more active and able to form complexes with olefins [11,12], thus facilitating their separation from saturated hydrocarbons through the membrane.

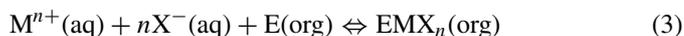
2. Mechanism and kinetic studies of SLM based separations

It is important that using simple H^+ concentration difference, it is possible to shift equilibrium of metal ion exchange in the donor and acceptor phases in different directions [13]. This creates concentration gradients of the ion-carrier complexes in the membrane and results in the directed transport of a metal from, for example, alkaline feed to a more acidic strip solution. After an ion exchange on another side of the membrane the carrier becomes protonated and diffuses back towards the donor phase. Evidently this simple cyclic mechanism can be used for active transport of a metal ion against its concentration gradient.

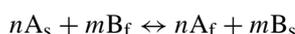
When the extractant exhibits acidic properties, coupled counter-transport takes place and the extraction reaction proceeds in the donor and acceptor phases according to the Eqs. (1) and (2):



However, when basic or neutral extractants are used, coupled coextraction takes place according to:



The transport process can be described as a pseudo chemical reaction. For example, for counter-transport of species A and B from the feed phase f to the strip phase s if they have different charges of the same sign we may write:



At an equilibrium we have

$$\begin{aligned} \mu_0(A) + nRT \ln a_{A_f} + \mu_0(B) + mRT \ln a_{B_s} \\ = \mu_0(A) + nRT \ln a_{A_s} + \mu_0(B) + mRT \ln a_{B_f} \end{aligned} \quad (4)$$

This equation can be rewritten as:

$$\left(\frac{[A]_f}{[A]_s} \right)^n = \left(\frac{[B]_f}{[B]_s} \right)^m \quad (5)$$

It means, for example, that in the case of copper transfer in exchange for two H^+ ions the separation or concentration factor of Cu^{2+} can reach 10^{20} if pH in feed and strip solutions are 10 and 0, respectively.

Separation and recovery of copper [14–18], zinc [19–21], nickel [22–24], alkali metals [25], precious metals [26–29], rare earth metals [30–34], etc., from aqueous technological solutions

and wastewater purification based on supported liquid membranes has intensively been studied. One of the problems is that when H^+ concentration difference is used as a driving factor to transfer metal ions, with time this difference decreases and the process stops. One of the possible ways to intensify the process is to conduct it in the presence of ammonia in the feed solution. In this case, a metal like Cu is extracted and transferred through the membrane from the complex with ammonia. The released NH_3 reacts with counter-transported H^+ and keeps pH in the feed practically constant [35]. As the result, it is possible to remove practically all Cu ions from the feed even if the initial concentration is as high as 160 g/l. If sulfuric acid is used as the stripping agent, with time Cu^{2+} concentration in it reaches solubility level and copper sulfate pentahydrate crystals are formed. The process can be used for regeneration of spent alkaline etching solutions, formed in big volumes as the result of printed circuit board production in microelectronic industry. Simultaneously copper sulfate crystals have quality comparable to a commercial chemical grade product. Stability of the membrane and the rates of Cu removal are high enough to make a process commercially feasible.

Rate of mass transfer in the case of HFSLM is controlled by three individual resistances, which are the resistance in a solution inside the fiber, across the membrane and outside the fiber. Often one of the three individual resistances will dominate the overall resistance. Normally, the flow through the tube side of hollow fibers is laminar and mass transfer coefficient (k_i) in the tube side could be estimated based on the Sherwood–Graetz correlation [16,36–42]

$$Sh = mGz^n \quad (6)$$

Sh and Gz are Sherwood number and Graetz number, respectively:

$$Sh = \frac{kd_i}{D} \quad (7)$$

$$Gz = \frac{d_i^2 v}{HD} \quad (8)$$

where d_i , H , D and v are inner diameter and the length of hollow fiber, diffusivity of interested species in the aqueous solution and linear velocity of the feed solution in the tube side, respectively.

Theoretically, for a diffusion process with fast chemical reaction, m can be from 1.62 [43] to 1.86 [44] and $n=0.33$. Slow chemical reactions with the carrier, membrane pore and module geometries could be potential factors responsible for the deviation of theoretical mass transfer coefficient from an experimental one. Modified correlations were proposed to overcome the deviations [37,39,45]. Typical values of k_i based on these correlations are in the range of 10^{-4} to 10^{-3} cm/s [42,46,47].

The diffusion of species through the membrane can be approximated by the diffusion through a cylindrical wall. The individual mass transfer coefficient k_m can be expressed as [48,49]:

$$k_m = \frac{\varepsilon D_m}{\tau^2 R_i \ln(R_o/R_i)} \quad (9)$$

where ε is the porosity of the hollow fiber membrane, τ the tortuosity of the hollow fiber membrane, R_o and R_i the outer and inner radius of the hollow fiber membrane and D_m is the diffusivity of the carrier complexes in the liquid membrane. Typical k_m in this case is in the range of 10^{-5} to 10^{-4} cm/s [38,50].

Mass transfer coefficient (k_o) in the shell side of hollow fiber module is described by various empirical correlations [36,40–42,47,51–55]. Results of these studies varied significantly due to more complex geometry of the system, the influence of module wall, the irregularity of fiber spacing and diameters, the fiber movement during operation, the inlet and outlet effects [52], possible channeling between fibers [54] and deformation of fibers during process. Nevertheless, the value of k_o in the shell side is around 10^{-3} cm/s [38,49,51,52] and can be additionally improved by a more efficient fiber arrangement and improved liquid flow patterns inside the module.

These estimated mass transfer coefficients based on empirical correlations together with experimentally determined values provide a useful tool for system modeling and scale-up of the corresponding membrane contactor process.

The theoretical description of facilitated transport across liquid membrane can be based on the assumption that the reactions of species with a carrier take place only on the membrane surface [56]. However, if the carrier is not very hydrophobic, it can leave the interior of membrane. In this case, the reactions take place mainly in the aqueous phase. Transport mechanisms in the two cases were called “small and big carousel”, respectively [56]. Equations for this situation without stirring and with stirring have been proposed [57]. It was also shown that the equations for the so-called “big carousel” may be simplified to the well-known transport equations with the reaction at the membrane/water interface, when the chemical reactions in the stagnant aqueous layers near the membrane surface are fast, and diffusion through the membrane or stagnant aqueous layer becomes the flux controlling processes.

3. Stability of SLM

Although SLMs have been widely studied for the separation and concentration of a variety of compounds and present many potential advantages over other separation methods, there have been very few large scale applications of SLM due to insufficient membrane stability. This problem can be due to the loss of the carrier and/or solvent from the membrane, which has an influence on both flux and selectivity. Time after which instability phenomena are observed varies from less than 1 h [58] to several months [59,60].

The major degradation mechanisms are:

- progressive wetting of the pores in the membrane support by the aqueous phase [61–63];
- pressure difference over the membrane [61,64];
- mutual solubility of species from the aqueous phase and liquid membrane phase [59,61,63,65];
- emulsion formation in the liquid membrane phase [63,66,67];
- blockage of membrane pores by precipitation of a carrier complex at the surface [68].

SLM stability can be affected by the type of polymeric support and its pore radius [69], organic solvent used in the liquid membrane, interfacial tension between the aqueous and membrane phase, flow velocity of the aqueous phases [67], and method of preparation [70].

The minimum transmembrane pressure required to push the impregnating phase out of the largest pores can be calculated using Laplace equation:

$$P_c = \frac{2\gamma \cos \theta}{r} \quad (10)$$

where γ is the interfacial tension between strip or feed solution and SLM phase, θ the contact angle between the membrane pores and the impregnating liquid, and r is the pore radius. Usually for commercial hollow fiber membrane contactors and hydrocarbon solvents P_c is much larger than transmembrane pressure, which indicates that pressure difference is not the main cause of SLM degradation [71]. It was proposed that only two mechanisms are the major important factors resulting in the membrane instability: the solubility of the SLM components in the adjacent feed or strip solutions and an emulsification of the SLM phase due to lateral shear forces.

Practically all the existing methods of measuring membrane liquid loss and determining water penetration into the membrane pores are destructive, that is after the determination the same SLM cannot be used again and has to be re-impregnated. One of the advantages of recently suggested impedance spectroscopy technique is that it is non-invasive and capable of providing continuous monitoring of SLM stability [72]. The effective area and thickness of an SLM change as the membrane liquid is lost, resulting in a change in the membrane capacitance and resistance.

Many efforts were spent to improve SLMs stability, such as:

1. Continuous reimpregnation of the support with liquid membrane phase, present as an emulsion in one of the aqueous solutions [73,74]. This regeneration of liquid membranes reminds biogenesis of cell membranes and it works well, but feed and/or strip solutions are still polluted with the membrane liquid.
2. Formation of barrier layers on a membrane surfaces, either by physical deposition [75] or by interfacial polymerization [76–79]. It works well to prevent emulsification of the membrane liquid in the aqueous solutions and to minimize displacement of liquid membrane solutions from the support pores by pressure difference over the membrane. However, the reproducibility of SLMs coated with the polymerized film is poor and the adhesion to the substrate is not strong. Besides that the additional layer can decrease the membrane permeability.
3. Stabilization of SLM by plasma polymerization surface coating [80]. It also reduces the size of the membrane surface pores and increases mass transfer resistance, resulting in a decreased permeability of the membrane system.

Recent developments in forming stable liquid membranes are promising although these approaches suffer from several

limitations and did not result in commercialization yet. Research activity should include more efforts in fundamental understanding of the role of a substrate and its structure in SLM preparation, and development of new solvents and/or carriers for SLM preparation [81].

4. New applications of SLM

There is a big review describing many experimental papers dealing with SLMs since 1970 until now [3,82]. After our general analysis we would like to mention that during the last several years more and more papers have described SLM based processes applicable for fine chemicals and even drugs. Evidently the possibility to produce value added products in relatively small volumes makes the SLM technology even more attractive for chemical and pharmaceutical industry.

As an illustration we give only a few examples. SLM can be used for the separation of citric and lactic acids in aqueous solutions [83]. The pores in the membrane support were filled with tri-*n*-octyl amine (TOA) and sodium carbonate was used as a strip solution. The feasibility of using SLM with hydrophobic liquid polyorganosiloxanes functionalized with amine, ether, ester and alkyl organo-functional groups in transport of lactic acid and ethyl lactate between aqueous phases was also reported [84]. The pH driven facilitated transport through both ether and amine functionalized polyorganosiloxane/celgard K-273 SLMs results in a dramatic permeability enhancement compared with that displayed by the free organic acid. The value of flux for an initial feed concentration of 10 g/l was 1.4×10^{-7} mol/(cm² s). Both amine and ether functionalized polyorganosiloxane based SLMs were stable for about 100 h. Valeric (*n*-pentanoic) acid extraction with Amberlite LA-2 (10 vol.%) in toluene (90 vol.%) is also possible [85]. Transport of aminoacids like phenylalanine through a SLM containing di-2-ethylhexylphosphoric acid (DEPHA) as a carrier in a spiral-channel module was studied and the effects of velocity of feed phase, initial feed concentration and the carrier concentration on the flux were determined [86]. Extraction of Penicillin G was carried out using two hollow fiber modules with organic phase containing a secondary amine Amberlite LA-2 as a carrier, 10% isodecanol as a modifier and kerosene as a diluent. The effects of initial feed concentration and carrier concentration on the kinetics of the complex mass transfer process were examined [87].

SLM can be used also for an increase of a concentration in analytical chemistry [88,89]. The advantages of SLM extraction over other methods for drugs and other substances determination are small sample volumes, short analysis time, low consumption of organic solvents for extraction, possibilities to work under physiological conditions and an excellent possibility for connection with various analytical instruments, possibly with automation of the whole process [90]. A technique based on a membrane extraction can be used for determination of drug–protein binding and was termed “equilibrium sampling through (ESTM)”. A basic solution of opipramol, noxyptyline, amitriptyline and diethazine was passed over the membrane and after enrichment the acceptor solution was analyzed by reversed-

phase high-performance liquid chromatography with UV detector. A porous PTFE membrane from Millipore with polyethylene backing was used with trioctylphosphine oxide (TOPO) as a carrier and with *n*-undecane and di-*n*-hexyl ether as organic solvents.

5. Summary

The SLM technology theoretically is one of the most efficient membrane based methods of separation. It does not use pressure or voltage but is based on difference of chemical energy as a driving factor of the process, for example, it can use simple H⁺ concentration difference. Coupled co- or counter-ion transport allows to get an active transport of the targeted species from diluted solutions into more concentrated and to collect toxic or precious species in a small volume of the acceptor solution. Sometimes, it is even possible to reach saturation of the strip solutions and finally precipitation of the product. Modern extractants make separation much faster due to facilitated transport and more selective due to their chemical specificity. Small volumes of extractant solutions and possibility to conduct continuous process make the SLM more attractive than classical ion exchange and solvent extraction technologies. Due to high diffusion coefficients in SLM it is possible to have ion extraction, transport and reextraction in one continuous technological step. Fluxes in many cases are higher than 10⁻⁸ mol/(cm² s) and are determined by carrier diffusion in the membrane. Recent development and commercialization of hydrophobic hollow fiber membrane contactors makes it possible to use them as a porous support and to reach high membrane surface per unit of volume with satisfactory membrane stability. High surface area of these systems gives the separation rates sufficient for industrial purposes. When the concentrated product forms saturated solution and then crystals, like in the mentioned earlier case of copper sulfate, the process does not result in any secondary waste and can be considered as a green chemistry process. The technology is easily scalable and payback time is decreased with the plant size increase. One can expect that SLM technology will find a lot of industrial applications in the near future.

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