Recent progress in supported liquid membrane technology: stabilization and feasible applications

Raffaele Molinari* and Pietro Argurio

Department of Chemical Engineering and Materials, University of Calabria Via P. Bucci, 44/A, I-87036 Rende (CS)-Italy

Abstract. Supported Liquid Membranes (SLMs) have been widely studied as feasible alternative to traditional processes for separation and purification of various chemicals both from aqueous and organic matrices. This technique offers various advantages like active transport, possibility to use expensive extractants, high selectivity, low energy requirements and minimization of chemical additives. SLMs are not yet used at large scale in industrial applications, because of the low stability. In the present paper, after a brief overview of the state of the art of SLM technology the facilitated transport mechanisms of SLM based separation is described, also introducing the small and the big carrousel models, which are employed for transport modeling. The main operating parameters (selectivity, flux and permeability) are introduced. The problems related to system stabilization are also discussed, giving particular attention to the influence of membrane materials (solid membrane support and organic liquid membrane (LM) phase). Various approaches proposed in literature to enhance SLM stability are also reviewed. Modification of the solid membrane support, creating an additional layer on membrane surface, which acts as a barrier to LM phase loss, increases system stability, but the membrane permeability, and then the flux, decrease. Stagnant Sandwich Liquid Membrane (SSwLM), an implementation of the SLM system, results in both high flux and stability compared to SLM. Finally, possible large scale applications of SLMs are also reviewed, evidencing that if the LM separation process is opportunely carried out (no production of by-products), it can be considered as a green process.

Keywords: supported liquid membrane; flux; selectivity; stability; application of liquid membranes

1. Introduction

Selective separation of organic and inorganic compounds from different matrices is a critical issue in the chemical industry. Conventional processes like solvent extraction, chemical precipitation, ion exchange, crystallization and fractional distillation are commonly used for this purpose. Most of these ones are energy consuming, produce a large amount of waste solvents and/or are discontinuous. Use of membrane-based separation processes represents a promising alternative to traditional processes, since they do not require high energy and chemical consumption (Hernández-Fernández *et al*. 2007), thus potentially resulting in sustainable separation processes.

Transport of organic and inorganic compounds across a liquid membrane (LM) is a powerful technology combining extraction and stripping into a one-step process, thus having great potential for reducing cost significantly. Liquid membrane systems include bulk liquid membrane, emulsion

---

* Corresponding author, Professor, E-mail: r.molinari@unical.it

liquid membrane and supported liquid membrane (SLM). Bulk liquid membranes usually consists of two aqueous phase (feed and strip) separated by a water-immiscible liquid membrane phase. The small membrane surface area per unit volume represents the most important drawback, making them not attractive by a technological point of view. Emulsion liquid membranes are characterized by a large surface area per unit source phase volume, which enhances the transport rate of this membrane. They can be thought as a bubble inside a bubble contained in the feed phase, where the inner bubble is the strip phase, closed by the LM membrane phase. ELMs are not technologically attractive mainly because of the low emulsion stability, so that if for any reason, the membrane does not remain intact during operation, the separation achieved to that point is destroyed.

SLMs have been studied in various fields like analytical, inorganic and organic chemistry, chemical engineering, biotechnology and biomedical engineering (Kocherginsky *et al*. 2007a, Molinari *et al*. 2009a, Molinari *et al*. 2009b). SLMs usually consist of an organic solvent impregnated in the pores of a hydrophobic microfiltration membrane and kept there by capillary forces (Kocherginsky *et al*. 2007a). This liquid membrane (LM) phase may also contain an extractant agent (carrier) which binds very selectively one or a class of components in the donor phase (feed), transporting it (or them) to the acceptor phase (strip) through the membrane, resulting in the so called facilitated transport (Molinari *et al*. 2006a). SLM systems combine mechanical resistance of solid membranes with selectivity of the extractant in the organic phase used in solvent extraction processes (Molinari *et al*. 2005).

SLMs have been studied in the transport of various cationic metals (Chaudry *et al*. 2008, Altin *et al*. 2010, Tarditi *et al*. 2008, Ata 2007) and anions (Güell *et al*. 2010) from wastewater, as well as different molecules of biological interest (Hassoune *et al*. 2009, Matsumoto *et al*. 2007, Muthuraman and Palanivelu 2006, Venkateswaran and Palanivelu 2006, Yang and Chung 2006) and organics (Ravanchi *et al*. 2010).

Common configurations of SLM are flat sheet and hollow fiber (Yang and Kocherginsky 2007). 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 have up to 220 m^2 area per module. Usually the LM phase is imbided in the pores of microporous hollow tubes and feed and strip solutions are circulated in the lumen and in the shell side of the hollow fibers, respectively (He 2008).

Potential advantages of SLMs in comparison to the convectional separation techniques, that make these processes interesting for a sustainable future, are: i) high separation factors; ii) higher flux or permeability compared to solid membranes since diffusion coefficients in liquids are at least three-four orders of magnitude higher than in solids; iii) very high selectivity, achievable when a proper selective complexing agent is chosen, thus obtaining a recovery and not a simple separation; iv) uphill concentration and separation, because of facilitated transport; v) expensive extractants can be used owing to their cyclical use; vi) minimization of chemical additives use, thus reducing the costs and the ecological impact of the treatment; vii) high feed/strip volume ratios; viii) ability to separate low concentration species from very dilute solutions, because of the effective binding; ix) high flexibility and easy scale up; x) low capital and operating costs.

Despite these advantages, SLMs are not yet used at large scale in industrial applications because of the insufficient system stability (Kemperman *et al*. 1996, Yang *et al*. 2007). This one varies from less than 1 hour to several months, depending on the system. Many studies have shown that one of the principal causes of instability is the loss of the LM phase (carrier and/or solvent) from the pores of the support followed by its substitution with feed and/or strip solutions, thus influencing both

flux and selectivity (Yang and Fane 1997, Zhang *et al.* 2001, Kemperman *et al.* 1998, Hill *et al.* 1996). This loss can be caused by one or a combination of various factors, like a pressure difference over the membrane (Danesi *et al.* 1987), solubility of the carrier and liquid membrane solvent in the adjacent feed and strip solutions (Zha *et al.* 1995), progressive wetting of the pores in the membrane support by the aqueous phases (Takeuchi *et al.* 1987), blockage of support pores by precipitation of carrier complex (Zhu and Li 1990), or emulsion formation (Neplenbroek *et al.* 1992a). Most likely, only two mechanisms are the major important factors resulting in membrane stability/instability: the solubility of the SLM components in the adjacent feed or strip solutions and an emulsification of the SLM phase caused by lateral shear forces. SLM stability can also be affected by the type of polymeric support, its pore radius, organic solvent used in the LM phase and method of preparation (Yang *et al.* 2007).

In this review the main theoretical aspects of transport in SLMs will be described, then some methods and techniques to stabilize SLMs will be examined and, finally, possible applications will be reported.

2. Theory

Solute permeation from feed to strip in SLM systems is obtained by means of a concentration difference of bound (and unbound) extractant existing between the two sides of the membrane generated by a chemical gradient of another species between feed and strip (facilitated coupled transport).

Two main transport mechanisms are known: facilitated coupled counter-transport and facilitated coupled co-transport (Fig. 1). In the first case, at feed–LM interface the carrier C selectively catches charged species A and releases the charged species B. The so formed AC complex diffuses through the LM where at LM–strip interface it releases A ion in the strip and binds B ion. The so formed CB complex diffuses back to the feed and the transport cycle begins again. A has the same charge as B, and the electrical neutrality is preserved because the carrier acts as a shuttle transporting A and B in opposite directions. This transport mechanism is typical for the transport of metal ions
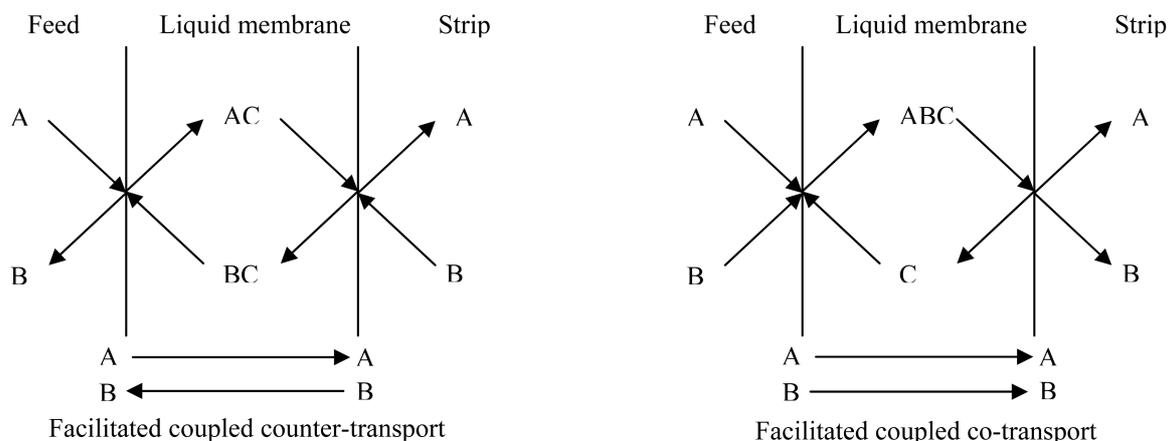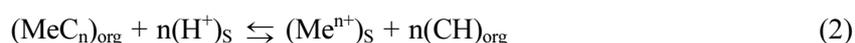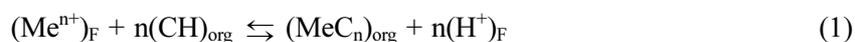

Fig. 1 Facilitated coupled transport of ionic solutes through a liquid membrane

(Me^{n+}) through the SLM with an acidic carrier CH (Molinari *et al.* 2006b), where the reaction scheme is the following

$$(Me^{n+})_F + n(CH)_{org} \leftrightarrows (MeC_n)_{org} + n(H^+)_F \tag{1}$$

$$(MeC_n)_{org} + n(H^+)_S \leftrightarrows (Me^{n+})_S + n(CH)_{org} \tag{2}$$

where the subscript 'F', 'org' and 'S' mean feed, organic and strip phases, respectively, and MeC_n is the metal ion–carrier complex.

In the case of facilitated coupled co-transport, a basic carrier like amines or phosphates is used to transport negatively charged species (A^{n-}) and usually H^+ as counter-ion across the membrane in the same direction. In that case at feed–LM interface the carrier C selectively catches the charged species A and the counter ion B, for the formation of ABC complex. This complex diffuses through the LM where at LM–strip interface it releases A and B ions in the strip. The so regenerated carrier molecule C diffuses back to the feed and the transport cycle begins again.

As a consequence of the coupling of the transport of A and B ions, the targeted ionic species can be transported across the LM against their concentration gradient. This so-called "uphill" or active transport will continue until the driving force (difference of chemical potentials of B ions (usually H^+) between feed and strip phases) is balanced by the difference of the chemical potentials of the targeted transported ions.

Transport of a solute across a SLM can be studied by the so-called "small carrousel" model. It is applicable when the targeted charged species are free (not complexed by counter ions) in the feed phase. This model is based on the assumption that the complexation and decomplexation reactions take place at well defined interfaces (feed/LM or LM/strip). According to this model the transport process of a solute A from feed to strip phases in SLM systems takes place in five steps in series: (1) solute diffusion from feed bulk to membrane surface, through liquid film adjacent to membrane; (2) reaction of chemical complexation of the solute by carrier at membrane surface feed side; (3) diffusion of the complex through the membrane thickness; (4) reaction of chemical decomplexation of the solute at membrane surface strip side; (5) solute diffusion from membrane surface (strip side) to strip bulk, through liquid film adjacent to the membrane.

When the targeted charged species are contained in the feed and strip phases in the form of relatively stable complexes (e.g., copper in ammonia solution) the reaction between this species and the carrier can be the limiting step and the more advanced "big carrousel" model have to be applied for system modeling (LeBlanc 1971). This mechanism is based on the idea that the carrier is able to diffuse from the organic into a thin aqueous layer where ion exchange reactions take place. This mechanism was applied in the case of copper removal from ammoniacal wastewater (Kocherginsky and Yang 2007b, Yang and Kocherginsky 2007) achieving a good agreement with the experimental data.

A fundamental parameter in the liquid-liquid extraction process is the distribution factor K_d. It is a key parameter of SLM separations, influencing both the permeation and process selectivity. It is defined as the ratio between the amount (moles) of a target species in organic and aqueous phases at equilibrium

$$K_d = \frac{(n_A)_{org}}{(n_A)_{aq}} \tag{3}$$

where A is the target component and the subscripts org and aq mean organic and aqueous phases,

respectively. When the organic and aqueous phase volumes are equal ($V_{org} = V_{aq}$), K_d can be expressed as follows

$$K_d = \frac{[A]_{org}}{[A]_{aq}} \tag{4}$$

Another important parameter, strictly related to the distribution factor, is the extraction percentage, defined as follows

$$E\% = \frac{(n_A)_{org}}{(n_A)_{in}} \times 100 = \frac{(n_A)_{org}}{(n_A)_{org} + (n_A)_{aq}} \times 100 = \frac{(n_A)_{org}}{(n_A)_{aq} \times \left[\frac{(n_A)_{org}}{(n_A)_{aq}} + 1\right]} \times 100 = \frac{K_d}{K_d + 1} \times 100 \tag{5}$$

where $(n_A)_{in}$ represents the initial amount (moles) of the target ionic species in the feed phase.

Selectivity can be calculated as the ratio $E\%(A) / E\%(B)$, where A is the target species and B represents another generic species contained in the aqueous phase. However, it must be noticed that previous selectivity considers only the extraction process and not also the permeation one. Thus it can be indicated as thermodynamic (static) or extraction selectivity (Molinari *et al*. 2006b). It can be quite different with respect to the transport (kinetic) selectivity, which must be determined by the ratio of the permeation flux J of the species of interest compared to another one (J_A / J_B).

The permeation flux is defined as the rate of mass transport of a solute through the membrane. It is the parameter frequently used to evaluate SLM performance (Singh *et al*. 2010). Calculation of fluxes can be done by using the following equation

$$J_A = \frac{V_F}{S_{exp} \cdot \varepsilon_m} \times \left(\frac{d[A]}{dt}\right)_F \tag{6}$$

where A represents the target species and V_F is the feed phase volume. S_{exp} is the membrane surface exposed to feed and strip phases. It is related to the effective membrane surface (S_{eff}) where transport really occurs by means of membrane porosity (ε_m): $S_{eff} = S_{exp} \varepsilon_m$.

The flux can be also calculated referring to strip concentration, thus considering only the recovered A

$$J_A = \frac{V_S}{S_{exp} \cdot \varepsilon_m} \times \left(\frac{d[A]}{dt}\right)_S \tag{7}$$

where V_S is the strip phase volume.

When diffusion of the carrier complex through the membrane is the limiting step, the permeation flux J can be calculated by an appropriate formulation of the Fick's first law of diffusion, as follows (Altin *et al*. 2010)

$$J_A = \frac{D}{L}([A]_{FI} - [A]_{SI}) = P([A]_{FI} - [A]_{SI}) \tag{8}$$

where D is the diffusion coefficient of the complex through the membrane phase, L is the membrane thickness and $[A]_{FI}$ and $[A]_{SI}$ are the concentrations of the target species at the membrane/feed interface and at the membrane/strip interface. P is the permeability; it is another parameter frequently used to evaluate SLM performance (Güell *et al*. 2010, Zidi *et al*. 2010).

Operating under efficient stripping conditions $[A]_{FI} \gg [A]_{SI}$ and ignoring the aqueous diffusion layer $[A]_{FI} \approx [A]_F$ (the complex diffusion in the membrane phase is the limiting step) and combining

Eqs. (6) and (8)

$$P = -\frac{V_F}{S_{eff}} \times \frac{d[A]_F}{dt} \frac{1}{[A]_F} \qquad (9)$$

Integrating Eq. (9) and assuming constant the permeability P, the following equation is obtained

$$\ln\left(\frac{[A]_F}{[A]_{F0}}\right) = -\frac{S_{eff}}{V_F} \cdot P \cdot t \qquad (10)$$

where $[A]_F$ and $[A]_{F0}$ are the concentrations of the target species in the aqueous feed phase at the time t and at the time 0 (initial feed concentration). This equation permits to evaluate the permeability (P) of the SLM system by plotting $\ln([A]_F / [A]_{F0})$ versus the time and determining the slope of the obtained straight line to calculate the permeability.

3. SLM stabilization

3.1 Membrane materials (solid support and LM phase) and modification of the support to achieve stable SLM

The characteristics of the membrane employed as support for SLM preparation influence both flux and stability: in principle higher porosity, thinner thickness and lower tortuosity of membrane matrix provide a higher flux. On the contrary, a membrane support with a thin and less tortuous structure is not favourable in terms of stability. The effects of these parameters on SLM stability were validated by Zidi *et al*. (2010). They studied the separation of phenol, one of the most important chemical pollutants in industrial wastewaters, contained in aqueous phase (200 mg L^{-1} of phenol at pH = 2) by a SLM system using tributyl phosphate (TBP) as the carrier. Two different flat polymeric supports were tested to evaluate membrane stability: i) Accurel® PP 2E-HF (Membrana, Germany), thickness = 160 mm, pore diameter = 0.2 μm, porosity = 75%, tortuosity = 1.29; ii) Durapore® PVDF (Millipore, USA), thickness = 120 μm, pore diameter = 0.2 μm, porosity = 65%, tortuosity = 1.43. Obtained phenol fluxes were 1.4 10^{-5} and 0.6 10^{-5} mol m^{-2} s^{-1} for Accurel and Durapore membrane, respectively, confirming that higher porosity and lower tortuosity provide a higher flux. Concerning system stability, results showed that transport efficiency of both polymeric supports decreased after 5 days of permanent operation without reimpregnation. The SLM prepared with the Durapore membrane was the best one in terms of stability: after 3 days of continuous run the transport efficiency declined of 17% against 54% of the Accurel membrane. This result also confirms the effect of polymeric support characteristic on SLM stability. Indeed the higher tortuosity and the lower porosity of Durapore membrane supports, with respect to Accurel one, result in better SLM stability.

Considering that chemical characteristics of the LM phase also influence SLM stability, Hernández-Fernández *et al*. (2007) proposed the use of Ionic Liquids (ILs) as LM phase. The prepared SLM was applied in the selective simultaneous separation of substrates and products of a transesterification reaction. ILs are organic salts that are liquids close to room temperature. Mainly they consist of an organic cation and a polyatomic inorganic anion (e.g., BF_4^-, PF_6^-). Use of an IL can potentially result in SLM stabilization because of its negligible vapor pressure, the possibility of minimizing its solubility in the surrounding phases by its adequate selection, and the greater capillary force associated

with its high viscosity, which could reduce its displacement from the pores of the membrane support. Besides ILs are characterized by high thermal stability, high ionic conductivity and non-flammability (de los Rios *et al*. 2007). Obtained results on the transesterification reaction products showed that permeability values were higher in the plain membranes (without LM phase) than in the SLM, owing to the additional mass-transfer resistance introduced by the high viscous LM phase. The plain membrane cannot be used for selective separations, while the situation changed dramatically when ILs were supported in the polymeric membranes. The SLM system was stable when tested over height continuous cycles of 48 hours, but stability was not tested in permeation tests because a simple immersion of the SLM in the feed and strip solvent (hexane) was carried out.

Despite the advantages in terms of selectivity and stability, use of ILs as LM phase presents various disadvantages, making it not suitable for large scale applications. First of all, the high viscosity of LM phase adds additional diffusive mass transfer resistance, resulting in relatively low fluxes. Moreover, because viscosity of ILs, the SLM preparation cannot be done by simple impregnation, but a repeated ultrafiltration of the ILs (at least three times) to force the liquid to enter into the pores of the membrane support under a nitrogen pressure of 2 bar is required. Besides, in the studied cases, the transport across the SLM using the ILs is not a facilitated transport, but a simple solution and diffusion. As a consequence, a not very high selectivity of separation is achievable, since: i) it is simply due to the difference in the partition coefficients of solutes and ii) the targeted species cannot be transported across the LM against its concentration gradient (no active transport). Finally, the reputation of ILs as "environmental friendly" has usually been justified with their negligible vapour pressure, but, even if ionic liquids will not evaporate and will not contribute to air pollution, most of them are water soluble and might enter the environment by this path. On these bases various studies conducted in last years demonstrated a not negligible toxicity of the ILs (Wang *et al*. 2011, Pham *et al*. 2010, Ma *et al*. 2010), making their application in SLMs not very eco-friendly in aqueous environment.

Various approaches have been proposed in literature to enhance SLM stability once membrane materials (solid support and/or LM phase), membrane morphology and/or operating conditions have been adequately chosen. Some of them permit to obtain promising results, but these approaches suffer from several severe limitations to their commercial viability. Continuous regeneration of LM works well, but feed and/or strip solutions are polluted with the liquid membrane phase (Takeuchi *et al*. 1990). Total or partial gelation of the LM phase to stabilize SLMs was studied by Kemperman *et al*. (1997) and by Neplenbroek *et al*. (1992b), but the poor reproducibility and the consideration that membrane coating with a gel layer seems not suitable for practical purpose, limits the application of this stabilization technique. SLM stabilization was also achieved by formation of barrier layers on a membrane surface, e.g., by interfacial polymerization or by plasma polymerization surface coating.

Indeed, Yang *et al*. (2007) proposed the development of a chemically modified P84 co-polyimide membrane as support for the preparation of stabilized SLM. In particular they prepared, via the phase inversion method, both symmetric and asymmetric flat membrane supports with high tortuosity by using the polyimide P84, polymer characterized by a number of attractive mechanical and physicochemical properties, as superior chemical resistance, giving it the potential to serve as the polymeric support matrix for SLM preparation. The prepared membranes were tested in Cu(II) permeability tests. Obtained results showed that the SLM made with the symmetric support matrix was much more stable than the asymmetric matrix, because the former may provide the formation of more stable stagnant layers than the latter. Initial copper(II) fluxes were 1.33×10^{-9} and 4.48×10^{-10} mol cm^{-2} s^{-1} for asymmetric and symmetric matrix, respectively, but the performance of both SLM
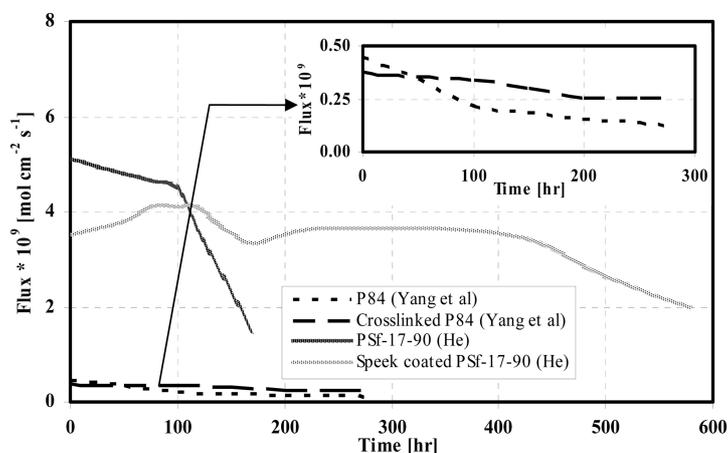
Fig. 2 Fluxes vs. time of SLMs assembled with original and modified membrane supports (elaborated from
      Yang *et al*. (2007) and He (2008))

deteriorated severely after 20-30 hour of operation. In particular, fluxes declined drastically (99% reduction after 28 hours operation) in the first day by using the asymmetric matrix, while it declined after 100 hours for the symmetric one. Matrix modification by interfacial chemical cross-linking with the aid of p-xylenediamine was conducted in order to enhance SLM stability. The SLM was first prepared by fully impregnating the support with the liquid membrane phase and then it was immersed into 10/90 wt% p-xylenediamine/water solution for preset time periods. Water was chosen instead of methanol because its immiscibility with the LM membrane phase, resulting in the induction of interfacial cross-linking reaction. Fluxes declined with the immersion time: best results were obtained by modifying the symmetric SLM; 10 min of chemical cross-linking resulted in a slightly decreased but acceptable flux ($3.78 \ 10^{-10}$ mol cm^{-2} s^{-1}). The results, schematized in Fig. 2, show that after 100 hours permeation time, the flux decreased by 52% for the unmodified membrane while only 10% for the modified one. After 280 hours, the fluxes decreased by 74% and 34% for the original and modified membranes, respectively. The overall work demonstrate that: i) symmetric structure of membrane support, ii) reduced surface pore sizes, iii) increased tortuosity, iv) increased membrane surface hydrophobicity and v) improved chemical resistance, due to matrix modification by interfacial chemical cross-linking, can improve SLM stability.

   He (2008) prepared a composite hollow fiber membrane made of polysulfone (PSf) coated with an ion exchange layer to achieve a stable SLM. PSf was the selected polymer because of its hydrophobic character, which makes it suitable to prepare supports for SLM, as well as its relatively high chemical resistance to concentrated inorganic acids, basic and saline solutions, and aliphatic hydrocarbons usually employed as organic solvent phase of LM. Besides, PSf has a relatively high surface tension, improving adhesion to the coating layer. By optimizing the spinning parameters bare PSf hollow fiber membrane supports were prepared; these ones were impregnated with the LM phase, and copper (II) permeation tests were carried out. Obtained initial flux was $5.1 \ 10^{-9}$ mol cm^{-2} s^{-1}, but the SLM showed an unsatisfactory stability (lower than 200 hours, Fig. 2). To improve system stability a sulfonated poly-(ether ether ketone) (SPEEK) layer was dip-coated on the outside surface of the hollow fiber membrane. SPEEK is a cation exchange polymer which is highly permeable to copper ion, but not to organic phase which is used in SLM. This hydrophilic layer should act as a

barrier against the organic phase (solvent and carrier) leakage from the SLM, resulting in increased system stability. The SPEEK composite membrane showed an initial copper flux a little lower than the unmodified PSf hollow fiber membrane (3.5 - 4.0 10^{-9} vs 5.1 $\times 10^{-9}$ mol cm^{-2} s^{-1}), but a stable permeation for about 400 h was achieved (see Fig. 2). Thus, the lower initial copper permeability is expected to be compensated by extended life time in copper extraction. As emphasized by the author, the coated polysulfone membrane had only one surface protected by the coating, thus the LM phase was still diffusing out from the other surface, resulting in unstable performance in SLM. On these basis the author suggests a double-layered composite membrane as a possibility to finally stabilize the SLM.

Summarizing, the results obtained by Yang *et al*. (2007) and by He (2008) (see Fig. 2) show an increase of system stability using an additional layer, but membrane permeability decreased.

3.2 Sandwich Liquid Membrane for obtaining simultaneous high flux and stability

Another possible approach to increase SLM stability, much more simple than that proposed by He (2008), consists in the development of a new LM configuration. Zhu and Li in 1990 observed a significant SLM lifetime enhancement using a "sandwich" liquid membrane but a very low flux with respect to the traditional SLM configuration was obtained. Starting from this idea, Kislik and Eyal in 1996 proposed a three compartments cell where two porous supports were used to separate the organic and aqueous phases. The organic solution containing the carrier was stirred or circulated in the middle compartment to decrease mass transfer resistance. They observed a significant SLM lifetime enhancement but the flux was very low, compared to traditional SLM configuration, because of the high thickness of the middle compartment, containing the LM phase, resulting in a relatively high transport resistance. The same authors developed another novel liquid membrane system, where the LM phase was substituted by a polyelectrolyte aqueous solution flowing between two ion exchange membranes, but the fluxes remained lower than that of the traditional SLM configuration (Kislik and Eyal 2000).

On these basis it was proposed (Molinari *et al*. 2002, Molinari *et al*. 2005, Molinari *et al*. 2006a) the use of a Stagnant Sandwich Liquid Membrane (SSwLM), where a stagnant thin liquid film (not stirred and not recirculated) of the LM phase was sandwiched between two thin hydrophilic membrane supports (Fig. 3).

This configuration was conceived with the intention to: i) increase system stability, with the two hydrophilic membrane supports acting as a barrier to LM phase loss, similar to what should happen in the double-layered composite membrane later proposed by He (2008); ii) increase the permeation flux, compared to the traditional SLM configuration, by minimising the total transport resistance that in many cases is caused by the friction in the pores and the tortuosity of the support. The SSwLM system was prepared by placing the organic solution, sonicated for 20 min to eliminate the
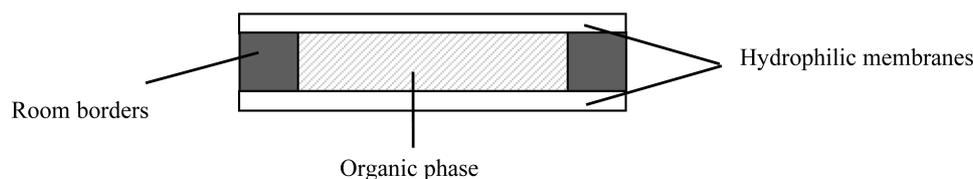

Fig. 3 Scheme of the Stagnant Sandwich LM

presence of air bubbles, inside a chamber with a volume of 58 μL and an initial thickness of 100 μm. This thickness was obtained by positioning a commercial triacetate sheet, on which a rectangular surface was opportunely cut out, between two hydrophilic membranes, so that the film acted as a spacer containing the organic liquid phase. The so assembled SSwLMs were tested in the separation of the drug Diclofenac (Molinari *et al*. 2006) and of copper(II) (Molinari *et al*. 2005) as organic and inorganic pollutants in water. Obtained results showed that using the SSwLM a clear stability enhancement was obtained with respect to the traditional SLM configuration, but the fluxes were low, especially in the case of Diclofenac, where ultrafiltration hydrophilic membrane as support, made of polyethersulfone (PES), were tested for SSwLM assembling.

In successive works (Molinari *et al*. 2009a, Molinari *et al*. 2009b) it was proposed the use of various microfiltration membranes for assembling the SSwLM system. These membranes were characterized by a wide pore size distribution and by a hydrophilic-lipophylic character. Particular attention was devoted to the orientation of the permeating module. In particular, when the module, and then the SSwLM, was horizontally positioned, a LM phase stratification on water droplets entered across the hydrophilic support happened (Fig. 4). The occurrence of this phenomenon did not influenced the extraction process, but it delayed the release of the target compound in the receiving phase. So, the vertical SSwLM orientation was adopted minimizing the previous problem.

In both copper and gemfibrozil (GEM, another drug different from Diclofenac) permeation, better results were obtained by using the SSwLM assembled with Supor® 200 membrane supports. The results, reported in Table 1 in terms of initial flux and stability, show that the SSwLM made with hydrophilic-lypophilic membrane supports achieved both higher flux and higher stability compared to the traditional SLM configuration.

The lower flux obtained in the case of GEM compared to copper was probably caused by the different viscosity of the LM phase formed by the different carrier molecules. In both cases the LM phase was a 30% v/v carrier concentration solution in the solvent n-decane; the carriers were di-(2-ethylhexyl) phosphoric acid (D2EHPA) used for copper and the more viscous tributylphosphate
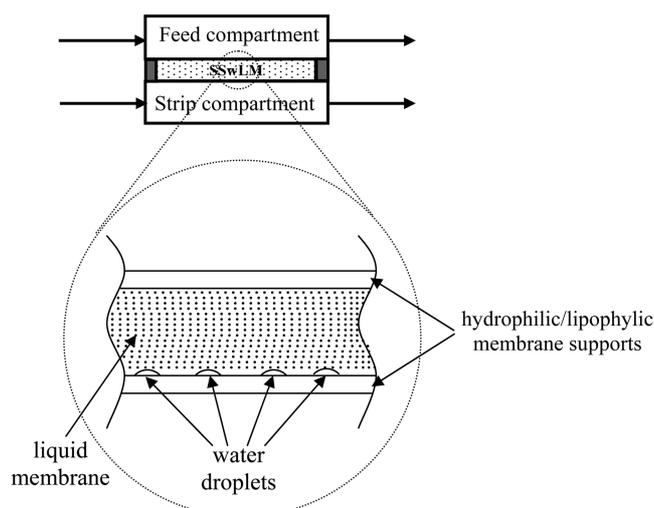

Fig. 4 Schematization of the permeation module and zoom on the SSwLM evidencing LM phase stratification on water droplets

Table 1 Comparison of flux and stability between SSwLM and SLM configurations

	Copper (II) *		GEM **	
	SLM	SSwLM	SLM	SSwLM
Flux (mol cm^{-2} s^{-1})	1.18 10^{-9}	1.52 10^{-9}	1.05 10^{-11}	2.39 10^{-11}
Stability (h)	49.2	183	23.5	336

* Molinari *et al*. (2009a); ** Molinari *et al* (2009b)

Table 2 Flux and stability of three LM systems assembled in various mode and tested in copper permeation

Type of system	LM phase	Flux (mol cm^{-2} s^{-1})	Stability (h)	Reference
SSwLM	D2EHPA 30% v/v in n-decane	1.52 10^{-9}	183	Molinari *et al*. (2009a)
SLM + Chem. mod. membr. surface	LIX 54 33% v/v in kerosene	3.78 10^{-10}	> 200	Yang *et al*. (2007)
SLM + SPEEK dip coating	LIX 84-I 20% v/v in dodecane	3.5 - 4.0 10^{-9}	400	He (2008)

(TBP) used for GEM transport, respectively. Concerning the different stability it could be ascribed to: i) different carrier used for preparing the LM to obtain the organic and inorganic separations, ii) different interaction of LM phases with the Supor 200 support, iii) different LM solubilities in water and iv) different viscosities, all influencing the LM phase loss. Total Organic Carbon (TOC) analyses of feed and strip phases evidenced a passage of the LM phase from the membrane phase to the adjacent feed and strip aqueous solutions in both cases, but it was lower in the case of GEM permeation. Higher LM phase release caused higher system destabilization.

In Table 2 the performance of the SSwLM system is compared, in terms of the main operating parameters flux and stability, with the results obtained by Yang *et al*. (2007) and by He (2008) by modifying the membrane supports used for SLM assembling. All data are obtained in copper(II) permeation tests. Best results were obtained by He *et al*. by using a SPEEK modified SLM. The SSwLM showed a little lower flux (same 10^{-9} order), but exhibited almost half stability. The chemical modification of the membrane surface proposed by Yang *et al* (2007) resulted in one order of magnitude lower flux (10^{-10} instead of 10^{-9}) and stability practically equal to that one obtained by using the SSwLM system.

As a general comparison among the three systems, it must be observed the different chemical behaviors of the materials and the chemical composition of the LM which can influence, also significantly, the described results. However, it must be noted the high simplicity in assembling the SSwLM using commercial membranes, compared to the chemical modification of the supports.

4. Possible applications of SLM

4.1 Environmental analyses

In assessment of ecological risk for chemical pollutants it is important to quantify the concentration of all analytes dissolved in aqueous samples at trace levels (Chimuka *et al*. 2004), that generally are

lower than the limit of detection of the analytical instruments. Thus, a separation and preconcentration step is required before the determination of analytes.

Conventional methods such as solid phase extraction and liquid-liquid extraction have been widely used, but they suffer of some drawbacks: they usually require high consumption of organic solvents, tedious procedure and time consuming work (See *et al.* 2010). Thus, solid-phase and liquid-phase micro-extraction were introduced to overcome these limitations.

Supported liquid membrane micro-extraction (SLMME) technique is a relatively new sample preparation technique that, recently, has attracted much interest in the field of environmental analysis (Es'haghi and Azmoodeh 2010). This technique was introduced as an improvement of liquid-phase microextraction as it provides high selectivity, flexibility, low operating cost and involves single operation step. This technique has been tested in the case of both organic (See *et al.* 2010, Chimuka *et al.* 2010) and inorganic analytes (Es'haghi and Azmoodeh 2010).

Critical parameters for applying this analytical technique are: pH of the sample (donor solution) and of the acceptor solutions, extraction time, extraction temperature, extracting solvent, stirring rate, ionic strength (salt concentration). These parameters must be optimized before the application of the supported liquid membrane microextraction technique (Chimuka *et al.* 2010).

Typical limits of detection, by using this preconcentration technique, are in the order of $10^{-1} - 1$ $\mu g\ L^{-1}$, as experimentally validated for the analyses of tap water and river water.

The possibility to detect analytes at concentration level of 10^{-1} $\mu g\ L^{-1}$, the good reproducibility (root square deviation RSD = 5-7 %), the high flexibility and low cost make the SLMME an interesting alternative to classical pre-concentration techniques for detecting analytes in liquid sample at trace levels. In particular, the SLMME is potentially applicable to verify compliance with the most restrictive legislation on drinking water standard, e.g. with the European standard for any pesticides, which has been set at 0.1 $\mu g\ L^{-1}$.

4.2 Wastewater treatment

In 2007 Yang and Kocherginsky studied the feasibility of a possible application of the SLM system such as the treatment of ammoniacal etching solutions, widely used in the electronic industry to etch a thin copper layer on electronic devices. As a consequence, a spent etching solution with copper(II) content up to 160 mg L^{-1} is formed. Traditionally this solution is submitted to neutralization and copper is precipitated. The generated ammoniacal wastewater still contains several ppm of copper and cannot be directly discharged. The predominant form of copper(II) ions in this wastewater is $[Cu(NH_3)_4]^{2+}$. Treatment of this ammoniacal solution using the SLM technology is potentially feasible and attractive. In particular, by using sulfuric acid as the stripping agent, copper(II) permeation takes place and its increasing concentration in the strip could reach a solubility level corresponding to copper precipitation as sulfate pentahydrate crystals with quality comparable to a commercial chemical grade product. Thus the separation process does not result in any secondary waste and can be considered as a green chemistry process.

In a previous work (Kocherginsky and Yang 2007b) the same authors demonstrated that concentration and recovery of copper from these ammoniacal complexes is possible by using a flat sheet SLM. However, the system was not suitable for practical application owing to its small membrane surface area (10 cm^2). On contrary, hollow fiber SLM represented a very attractive solution to apply SLM for copper removal from industrial ammoniacal wastewater. The results obtained by using a Liqui-Liqui-Cel® 2.5 in.×8 in. membrane contactor (1.4 m^2 membrane area) operated at a flow rate of 4 L

h^{-1} showed that copper level in the ammoniacal solution was reduced to less than 5 ppm. The treated solution can be reused as rinse water for printed circuit boards (PCB) production or discharged directly in compliance with the environmental regulations. Results also evidenced the selectivity in copper(II) separation over other cations (copper separation factors of 103, 17 and 3.8 over cadmium(II), zinc(II) and nickel(II), respectively). SLM stability was evaluated by monitoring the overall mass transfer coefficient in the time of the hollow fiber membrane contactor operating in co-current mode and same flow rate in the lumen (feed wastewater) and shell (strip solution) in order to obtain a stable SLM. The results showed a transport efficiency which decreased by half in the first half month and then it was practically constant. The membrane could be washed, dried, reimpregnated and then reused. This possibility of hollow fiber membrane contactor reuse is important in terms of economical sustainability.

Guell *et al*. (2010) proposed the application of a SLM system in the speciation (separation) of arsenic species in environmental matrices which is one of the most important applications involving As separation. A solution containing equal amount of As(III) and As(V) species was used as the feed phase and Aliquat 336 in dodecane, modified with 4% dodecanol, was the LM phase. The results showed that the speciation was possible, because As(V) was quantitatively transported across the SLM after 6 h decreasing to ppb level in the feed, whereas no As(III) transport in the strip was observed. This selectivity was caused by the different kinetics of As(III) and As(V) complexation by the carrier. Indeed the As(V)–Aliquat 336 system is kinetically more favorable than the As(III) system. To test the possible SLM application in As speciation from real matrices, solutions prepared by dissolving As species in tap water and natural river water were submitted to SLM separation. The results confirmed SLM applicability but some difficulties were encountered when an As level of 280 mg L^{-1}, typical of polluted groundwater, was considered. Indeed, using synthetic wastewater, prepared with Milli-Q water, a 100% As(V) recovery was achieved after 6h while using tap water as matrix, the recovery decreased to 44%, probably because of the presence of other interfering anions in the solution.

The results obtained by Yang and Kocherginsky (2007) and by Guell *et al*. (2010) demonstrated that the SLM system represents an effective way to concentrate and recover inorganic (metallic) ions from industrial wastewaters. In particular transport at ppb levels as well the separation of metallic ions both of different species (Cu(II) from Cd(II), Zn(II) and Ni(II)) and of different oxidation states (As(V) from As(III)) were achievable.

4.3 Remediation of nuclear waste

Traditionally in the closed nuclear fuel cycle the recovery of U and Pu produces a stream containing minor actinides, while fission/activation products (e.g., U, Pu, Am, Eu, Sr) and process/ structural materials (Fe, Ni, Cr, etc.) are concentrated in high level waste (HLW). This concentrate is usually submitted to immobilization in glass/ceramic matrices disposed in geological repositories. Considering the half lives of the fission products (in the range of hundred-millions years) this solution results unsustainable. The treatment of HLW by SLM represents a possible alternative.

On these basis Ansari *et al*. (2007) evaluated the possibility to use SLM in the remediation of HLW. Obtained results showed that Am(III), Eu(III), Pu(IV), Np(IV) and U(VI) were quantitatively recovered from nitric acid solution by using the facilitated SLM transport. The transport rates were marginally affected by the presence of Fe(III) as structural material.

In order to effectively use the SLM system for the separation of metal ions from HLW, the
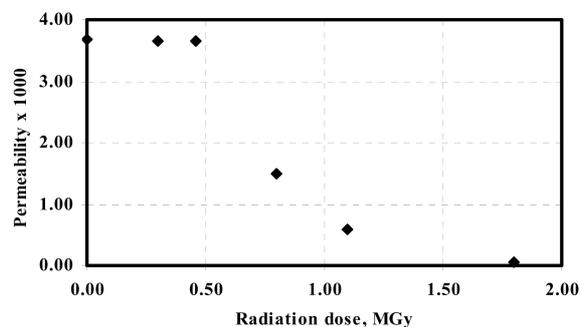
Fig. 5 Permeability vs radiation dose for Am(III) transport across the SLM used (from Ansari el al. (2007))

radiolytic stability of the liquid membrane phase has to be considered. The results, obtained by increasing the radiation dose from 0 MGy to 1.8 MGy, evidenced no significant decrease of the permeability of Am(III) when the radiation dose was lower than 0.46 MGy. However the permeability decreased almost linearly by increasing the radiation dose from 0.46 to 1.8 MGy (Fig. 5).

Two factors were responsible of this behavior: i) the capability of the LM phase to extract Am(III) decreased linearly with the irradiation dose, because the carrier was degraded; ii) the density of the LM phase was almost insensitive to the dose, but the viscosity increased with the irradiation dose, affecting the transport behavior. This phenomenon is indicated as radiolytic degradation of the LM phase.

Along this research topic, in 2010 Singh *et al.* considered the permeation of U(VI) from phosphoric acid medium across a SLM. The influence of various parameters, as feed acidity, nature of the stripping solution, carrier concentration, membrane pore size and thickness was studied. The results confirmed that membrane support characteristics affect the transport of the target ionic species (such as U(VI)) as reported in the previous sections, and showed that U(VI) separation from phosphoric acid medium by SLM is feasible. System stability was studied by performing ten continuous experimental cycles with 6 hours duration each. The results evidenced a good operational stability, with a quite linear decrease of the permeation performance, for the first eight cycles. The percentage of permeation decreased drastically with the 10th cycle.

5. Conclusions

In this brief review the recent developments in SLM technology, by pointing out on the main parameters such as flux, stability and selectivity, have been discussed. Thanks to the coupled active transport, the SLM can work as a matter pump, transporting the target ionic species from diluted to concentrated solutions. Despite the significant advantages of SLMs with respect to traditional separation techniques, they are not yet largely used at industrial level because of their low stability, essentially caused by LM phase loss out of the pores of membrane supports.

Various approaches have been described in this review for SLM stabilization: operating on membrane materials (LM phase (e.g., solvent) or support) and/or by developing novel system configuration. Use of ionic liquids as LM phase seems attractive in terms of system stability, thanks to their negligible vapor pressure and their low solubility in the liquid phase adjacent the SLM, but their high viscosity

and their not negligible toxicity, make their application not very eco-friendly.

In last years some authors proposed the surface modification of membrane supports by: i) dip coating hydrophilic layer; ii) chemical surface modification to reduce the surface pore size or to enhance surface hydrophobicity, thus increasing system stability. It was evidenced that the presence of an additional layer on the membrane support acts as a barrier against LM phase loss increasing system stability, but membrane permeability decreased because the increase of the mass transfer resistance. Stagnant Sandwich Liquid Membrane (SSwLM) was an implementation of the SLM system responding to the need to obtain both high flux and stability. Best results were obtained both in terms of flux (J = 3.5 - 4.0 10^{-9} mol cm^{-2} s^{-1}) and stability (400 hours) by dip coating a hydrophobic layer on membrane support surface. The SSwLM showed a little lower flux (1.52 $\times 10^{-9}$ mol cm^{-2} s^{-1}), and exhibited almost half stability. The chemical modification of the membrane surface resulted in one order of magnitude lower flux (10^{-10} instead of 10^{-9}) and stability practically equal to that one obtained by using the SSwLM system. The high simplicity in assembling the SSwLM using commercial membranes, compared to the difficulty of chemical modification of the supports, represents from a practical point of view, a not negligible advantage of this SLM system.

Concerning applications, the SLM technique is today largely employed in the field of environmental analysis as a new sample preparation technique to concentrate the analytes contained in aqueous samples at trace levels before the analytical determination.

The treatment of spent etching solution of the electronic industry, with the SLM technique, has been proposed and technically validated in literature as possible large scale application. Results evidenced reduction of copper(II) level lower than regulation limits. Process selectivity and stability were high enough to candidate the SLM process as effective for concentrating and recovering copper ion from industrial wastewater also when the predominant form of metal ion in this wastewater was a moderate strong complex. This separation process did not produce by-products and can be considered as a green process.

Another example of application of the SLM technique is the remediation of nuclear waste, but the radiolylic stability of the LM phase in addition to the operational stability, has to be opportunely considered.

It is expected that a still little research effort could make the SLM technique be applied in a not so far future as an effective way to separate, concentrate and purify inorganic and organic solutes from various types of media fulfilling sustainability criteria.

References

Altin, S., Yildirim, Y. and Altin, A. (2010), "Transport of silver ions through a flat-sheet supported liquid membrane", *Hydrometallurgy*, **103**(1-4), 144-149.

Ansari, S.A., Mohapatra, P.K., Prabhu, D.R. and Manchanda, V.K. (2007), "Evaluation of N,N,N',N'-tetraoctyl-3-oxapentane-diamide (TODGA) as a mobile carrier in remediation of nuclear waste using supported liquid membrane", *J. Membrane Sci.*, **298**(1-2), 169-174.

Ata, O.N. (2007), "Mathematical modelling of unsteady-state transport of metal ions through supported liquid membrane", *Hydrometallurgy*, **87**(3-4), 148-156.

Chaudry, M.A., Bukhari, N. and Mazhar, M. (2008), "Coupled transport of Ag(I) ions through triethanolamine–cyclohexanone-based supported liquid membranes", *J. Membrane Sci.*, **320**(1-2), 93-100.

Chimuka, L., Cukrowska, E. and Jönsson, J.Å. (2004), "Why liquid membrane extraction is an attractive alternative in sample preparation", *Pure Appl. Chem.*, **76**(4), 707-722.

Chimuka, L., Msagati, T.A.M., Cukrowska, E. and Tutu, H. (2010), "Critical parameters in a supported liquid membrane extraction technique for ionizable organic compounds with a stagnant acceptor phase", *J. Chromatogr. A*, **1217**(16), 2318-2325.

Danesi, P.R., Reichley-Yinger, L. and Rickert, P.G. (1987), "Lifetime of supported liquid membranes: the influence of interfacial properties, chemical composition and water transport on the long term stability of the membranes", *J. Membrane Sci.*, **31**(2-3), 117-145.

de los Ríos, A.P., Hernández-Fernández, F.J., Tomás-Alonso, F., Palacios, J.M., Gómez, D., Rubio, M. and Víllora G. (2007), "A SEM–EDX study of highly stable supported liquid membranes based on ionic liquids", *J. Membrane Sci.*, **300**(1-2), 88-94.

Es'haghi, Z. and Azmoodeh, R. (2010), "Hollow fiber supported liquid membrane microextraction of Cu^{2+} followed by flame atomic adsorption spectroscopy determination", *Arab. J. Chem.*, **3**(1), 21-26.

Güell, R., Fontàs, C., Salvadó, V. and Anticó, E. (2010), "Modelling of liquid–liquid extraction and liquid membrane separation of arsenic species in environmental matrices", *Sep. Purif. Technol.*, **72**(3), 319-325.

Hassoune, H., Rhlalou, T. and Verchère, J.F. (2009), "Mechanism of transport of sugars across a supported liquid membrane using methyl cholate as mobile carrier", *Desalination*, **242**(1-3), 84-95.

He, T. (2008), "Towards stabilization of supported liquid membranes: preparation and characterization of polysulfone support and sulfonated poly (ether ether ketone) coated composite hollow fiber membranes", *Desalination*, **225**(1-3), 82-94.

Hernández-Fernández, F.J., de los Ríos, A.P., Rubio, M., Tomás-Alonso, F., Gómez, D. and Víllora, G. (2007), "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. Membrane Sci.*, **293**(1-2), 73-80.

Hill, C., Dozol, J.F., Rouquette, H., Eymard, S. and Tournois, B. (1996), "Study of the stability of some supported liquid membranes", *J. Membrane Sci.*, **114**(1), 73-80.

Kemperman, A.J.B., Bargeman, D., van den Boomgaard, Th. and Strathmann, H. (1996), "Stability of supported liquid membranes: state of the art", *Sep. Sci. Technol.*, **31**(20), 2733-2762.

Kemperman, A.J.B., Damink, B., van den Boomgaard, Th. and Strathmann, H. (1997), "Stabilization of supported liquid membranes by gelation with PVC", *J. Appl. Polym. Sci.*, **65**(6), 1205-1216.

Kemperman, A.J.B., Rolevink, H.H.M., Bargeman, D., van den Boomgaard, Th. and Strathmann, H. (1998), "Stabilization of supported liquid membranes by interfacial polymerization top layers", *J. Membrane Sci.*, **138**(1), 43-55.

Kislik, V.S. and Eyal, A.M. (1996), "Hybrid liquid membrane (HLM) and supported liquid membrane (SLM) based transport of titanium(IV)", *J. Membrane Sci.*, **111**(2), 273-281.

Kislik, V.S. and Eyal, A.M. (2000), "Aqueous hybrid liquid membrane process for metal separation. Part II. Selectivity of metals separation from wet-process phosphoric acid", *J. Membrane Sci.*, **169**(1), 133-146.

Kocherginsky, N.M., Yang, Q. and Seelam, L. (2007a), "Recent advances in supported liquid membrane technology", *Sep. Purif. Technol.*, **53**(2), 171-177.

Kocherginsky, N.M. and Yang, Q. (2007b), "Big Carrousel mechanism of copper removal from ammoniacal wastewater through supported liquid membrane", *Sep. Purif. Technol.*, **54**(1), 104-116.

LeBlanc, O.H. (1971), "The effect of uncouplers of oxidative phosphorylation on lipid bilayer membranes: carbonylcyanidem-chlorophenylhydrazone", *J. Membrane Biol.*, **4**(1), 227-251.

Ma, J.M., Cai, L.L., Zhang, B.J., Hu L.W., Li, X.Y. and Wang, J.J. (2010), "Acute toxicity and effects of 1-alkyl-3-methylimidazolium bromide ionic liquids on green algae", *Ecotox. Environ. Safe.*, **73**(6), 1465-1469.

Matsumoto, M., Ohtani, T. and Kondo, K. (2007), "Comparison of solvent extraction and supported liquid membrane permeation using an ionic liquid for concentrating penicillin G", *J. Membrane Sci.*, **289**(1-2), 92-96.

Molinari, R., Pirillo, F. and Argurio, P. (2002), "Sandwich liquid membrane in the separation and concentration of Cu^{2+}", *Ann. Chim. (Rome, Italy)*, **92**(10), 973-982.

Molinari, R., Argurio, P. and Pirillo, F. (2005), "Comparison between stagnant sandwich and supported liquid membranes in copper(II) removal from aqueous solutions: flux, stability and model elaboration", *J. Membrane Sci.*, **256**(1-2), 158-168.

Molinari, R., Caruso, A., Argurio, P. and Poerio, T. (2006a), "Diclofenac Transport through Stagnant Sandwich and Supported Liquid Membrane Systems", *Ind. Eng. Chem. Res.*, **45**(26), 9115-9121.

Molinari, R., Poerio, T. and Argurio, P. (2006b), "Selective removal of Cu^{2+} versus Ni^{2+}, Zn^{2+} and Mn^{2+} by using a new carrier in a supported liquid membrane", *J. Membrane Sci.*, **280**(1-2), 470-477.

Molinari, R., Argurio, P. and Poerio, T. (2009a), "Studies of various solid membrane supports to prepare stable sandwich liquid membranes and testing copper(II) removal from aqueous media", *Sep. Purif. Technol.*, **70**(2), 166-172.

Molinari, R., Argurio, P. and Poerio, T. (2009b), "Flux enhancement of stagnant sandwich compared to supported liquid membrane systems in the removal of Gemfibrozil from waters", *J. Membrane Sci.*, **340**(1-2), 26-34.

Muthuraman, G. and Palanivelu, K. (2006), "Transport of textile dye in vegetable oils based supported liquid membrane", *Dyes Pigments*, **70**(2), 99-104.

Neplenbroek, A.M., Bargeman, D. and Smolders, C.A. (1992a), "Mechanism of supported liquid membrane degradation—emulsion formation", *J. Membrane Sci.*, **67**(2-3), 133-148.

Neplenbroek, A.M., Bargeman, D. and Smolders, C.A. (1992b), "Supported liquid membranes—stabilization by gelation", *J. Membrane Sci.*, **67**(2-3), 149-165.

Pham, T.P.T., Cho, C.W. and Yun, Y.S. (2010), "Environmental fate and toxicity of ionic liquids: A review", *Water Res.*, **44**(2), 352-372.

Ravanchi, M.T., Kaghazchi, T. and Kargari, A. (2010), "Facilitated transport separation of propylene–propane: Experimental and modeling study", *Chem. Eng. Process.*, **49**(3), 235-244.

See, H.H., Hauser, P.C., Sanagi, M.M. and Ibrahim, W.A.W. (2010), "Dynamic supported liquid membrane tip extraction of glyphosate and aminomethylphosphonic acid followed by capillary electrophoresis with contactless conductivity detection", *J. Chromatogr. A*, **1217**(37), 5832-5838.

Singh, S.K., Misra, S.K., Tripathi, S.C. and Singh, D.K. (2010), "Studies on permeation of uranium (VI) from phosphoric acid medium through supported liquid membrane comprising a binary mixture of PC88A and Cyanex 923 in n-dodecane as carrier", *Desalination*, **250**(1), 19-25.

Takeuchi, H., Takahashi, K. and Goto, W. (1987), "Some observations on the stability of supported liquid membranes", *J. Membrane Sci.*, **34**(1), 19-31.

Tarditi, A.M., Marchese, J. and Campderrós, M.E. (2008), "Modelling of zinc (II) transport through a PC-88A supported liquid membrane", *Desalination*, **228**(1-3), 226-236.

Venkateswaran, P. and Palanivelu, K. (2006), "Recovery of phenol from aqueous solution by supported liquid membrane using vegetable oils as liquid membrane", *J. Hazard. Mater.*, **131**(1-3), 146-152.

Yang, Q. and Chung, T.S. (2006), "Modification of the commercial carrier in supported liquid membrane system to enhance lactic acid flux and to separate l,d-lactic acid enantiomers", *J. Membrane Sci.*, **294**(1-2), 127-131.

Yang, Q., Chung, T.S., Xiao, Y. and Wang, K. (2007), "The development of chemically modified P84 co-polyimide membranes as supported liquid membrane matrix for Cu(II) removal with prolonged stability", *Chem. Eng. Sci.*, **62**(6), 1721-1729.

Yang, Q. and Kocherginsky, N.M. (2007), "Copper removal from ammoniacal wastewater through a hollow fiber supported liquid membrane system: Modeling and experimental verification", *J. Membrane Sci.*, **297**(1-2), 121-129.

Yang, X.J. and Fane, T. (1997), "Effect of membrane preparation on the lifetime of supported liquid membranes", *J. Membrane Sci.*, **133**(2), 269-273.

Wang, H., Malhotra, S.V. and Francis A.J. (2011), "Toxicity of various anions associated with methoxyethyl methyl imidazolium-based ionic liquids on Clostridium sp.", *Chemosphere*, **82**(11), 1597-1603.

Zha, F.F., Fane, A.G. and Fell, C.J.D. (1995), "Instability mechanisms of supported liquid membranes in phenol transport process", *J. Membrane Sci.*, **107**(1-2), 59-74.

Zhang, B., Gozzelino, G. and Baldi, G. (2001), "Membrane liquid loss of supported liquid membrane based on n-decanol", *Colloid. Surfaces A*, **193**(1-3), 61-70.

Zhu, G. and Li, B. (1990), "A study of water uptake in supported liquid membranes", *Water Treatment*, **5**, 150-156.

Zidi, C., Tayeb, R., Ali, M.B.S. and Dhahbi M. (2010), "Liquid–liquid extraction and transport across supported liquid membrane of phenol using tributyl phosphate", *J. Membrane Sci.*, **360**(1-2), 334-340.

CC