CHAPTER 3

Supported Liquid Membranes and Their Modifications: Definition, Classification, Theory, Stability, Application and Perspectives

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Nomenclature

α_f	fraction of the transported substance that is extractable from the feed phase
α_s	fraction of the transported substance that is extractable from the strip phase
$\Delta C_{CS,m}$	concentration gradient of carrier-substance complex in the membrane
ε	porosity
γ_i	activity coefficient of the *i*th species
η	viscosity of the organic phase
μ_i	chemical potential of the *i*th species
θ	contact angle between the membrane pores and the membrane liquid
τ	tortuosity
Ab	antibody
Ab-Ag	antibody-antigen complex
Ag	antigen
C	concentration
C_f	total concentration in the feed phase
C_i	concentration of the *i*th species
C_s	total concentration in the strip phase
$C_{S,o}$	initial concentration of transported substance
D	diffusion coefficient
d	membrane thickness

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D_{CS}	diffusion coefficient of carrier-substance complex
D_m	diffusion coefficient in membrane phase
D_o	diffusion coefficient in bulk solution
D_{SLM}	supported liquid membrane diffusion coefficient
E	extraction efficiency
E_e	concentration-enrichment factor
$E_{e(max)}$	maximum concentration-enrichment factor
J	flux
k	Boltzmann constant
K_a	dissociation constant
K_{aff}	affinity constant
K_{ext}	extraction constant
K_f	partition coefficient between organic phase and feed phase
k_m	mass-transfer coefficient
K_m	partition coefficient
K_s	partition coefficient between strip and membrane phase
L_m	ligand located in the membrane phase
n_f	total amount of extracted compound in the feed phase
n_s	total amount of extracted compound in the strip phase
n_w	total amount of extracted compound in the waste phase
P	permeability
P_c	transmembrane pressure
R	recovery
r	pore radius
r_s	molecular radius of the solute
SL_m	ligand-substance complex in membrane phase
S_m	substance located in the membrane phase
T	temperature
V_f	volume of the feed phase
V_s	volume of the strip phase

Abbreviations

AMPA	(aminomethyl)phosphonic acid
Armak	Armak, Chicago, MI, USA
Ashai Kasei	Ashai Kasei Corp., Tokyo, Japan
β-CD	β-cyclodextrin
BEHA	bis(2-ethylhexyl)-amine
BF_4	tetrafluoroborate
BMIM	1-butyl-3-methylimidazolium
Celanese	Celanese Plastic, Dallas, TX, USA
CTA	cellulose triacetate
DAE	diaminoethane
DBSA	dodecylbenzylsulfonic acid

DC18C6	dicyclohexano-18-crown-6
DEHPA	di-2-ethylhexyl phosphoric acid
DETA	diethylenetriamine
DEYA	diethylamine
DNB	dinitrobenzoyl
DNNS	dinonylnaphthalenesulfonic acid
DOP	dioctylphthalate
DOS	dioctylsebacate
DOTP	bis(2-ethylhexyl)terephthalate
DTPA	diethylenetriaminepentaacetic acid
Enka	Enka Produktgruppe Membrana, Wuppertal, Germany
Flow Lab.	Flow Laboratories, Rickmansworth, UK
FL-SLM	flat-sheet SLM
Gore	W. L. Gore & Associates, Inc., Newark, DE, USA
HF	hollow fiber
HF-SLM	hollow-fiber SLM
HLB	hydrophilic-lipophilic balance
Millipore	Millipore, Billerica, MA, USA
Mitzubishi Rayon	Mitzubishi Rayon Company, Otake, Japan
NPOE	*o*-nitrophenyloctylether
NTf_2	bis(trifluoromethanesulfonyl)imide
Nucelopore Corp.	Nucelopore Corp., Pleasanton, CA, USA
O/W	oil/water
OMIM	1-octyl-3-methylimidazolium
PE	polyethylene
PEHFSD	pseudoemulsion-based hollow-fiber strip dispersion
PF_6	hexafluorophosphate
PIM	polymer inclusion membranes
Polyplastics	Polyplastics Taiwan Co., Ltd, Taipei, Taiwan
PP	polypropylene
PPG	polypropylene glycol
PTFE	poly(tetrafluoroethylene)
PTSA	*p*-toluenesulfonic acid
PVC	poly(vinyl chloride)
PVDF	polyvinylidene fluoride
SDHLM	strip dispersion hybrid liquid membrane
SLM	supported liquid membrane
SPE	solid-phase extraction
Sumimoto	Sumimoto Chemical, Tokyo, Japan
TBEP	tri(butoxyethyl)phosphate
t-BuDC18C6	*t*-butyldicyclohexano-18-crown-6
TEHP	tris(2-ethylhexyl)phosphate
TOMA-Cl	trimethylammonium chloride
TOPO	trioctylphosphine oxide

1. Introduction

A supported liquid membrane (SLM) is one of the three-phase liquid membrane systems in which the membrane phase (liquid) is held by capillary forces in the pores of microporous polymeric or inorganic film. The immobilized liquid is a membrane phase and a microporous film serves as a support for the membrane. Usually SLMs are based on hydrophobic organic solvent immobilized in a polymeric membrane separating two aqueous solutions. In some cases, the arrangements are opposite and the pores in the support separating two nonaqueous phases are impregnated by water. The problem with this arrangement is that water has relatively high volatility and such membranes are not stable, but this problem can be solved using ionic liquids (ILs) as a membrane phase. An SLM can also be formed by immobilizing the membrane phase between two nonporous films which are permeable to transported substances and usually nonselective. The latter is much more stable, but is less suitable due to a higher mass-transfer resistance of the nonporous layer, because the diffusion coefficient (D) value in liquids is at least three or four orders of magnitude higher than in solid polymer membranes. Other types of liquid membranes, polymer inclusion membranes (PIMs) and gelled liquid membranes, have been investigated to improve SLM stability. These types of membranes are formed either by casting the solution of polymer, usually cellulose triacetate (CTA) or poly (vinyl chloride) (PVC), and plasticizer (solvent characterized by high viscosity) to form a thin, flexible and stable film (self-supporting PIM) or by liquid-phase gelation in the PVC pores of an SLM.

SLM was reported for the first time by Scholander [1] who used thin cellulose acetate filters impregnated with an aqueous hemoglobin solution for oxygen transport. A similar system was reported by Wittenberg [2] for studying the molecular mechanism of oxygen transport. In the 1960s and 1970s, the liquid membrane concept was mostly used in emulsion liquid membranes, when Li [3] patented their application for hydrocarbons separation. However in the beginning of the 1980s, there was an increase of research interest in the supported liquid membrane as SLMs are easier to implement into a continuous flow system. Since then SLMs have been used to solve an increasing number of separation problems, including metals and organic compounds separation and the resolution of stereoisomers. The unique flexibility and ease of preparation of SLMs in various configurations, despite some stability and lifetime problems, has resulted in their application in many, sometimes very different fields where selective and efficient separation methods are necessary: in hydrometallurgy, biotechnology, wastewater treatment, the capture of greenhouse gases, analytical and environmental chemistry, and in the pharmaceutical industry.

In this chapter, the principle, kinetic and transport mechanisms, stability, SLM design and configuration are presented. Moreover, selected applications of SLMs and future perspectives are discussed.

2. Supported Liquid Membrane Separation Technique—the Principle

Liquid membrane separation combines the solvent extraction and stripping processes (re-extraction) in a single step. The great potential for energy saving, low capital and operating cost, and the possibility to use expensive extractants, due to the small amounts of the membrane phase, make SLMs an area deserving special attention.

The principles and applications of SLM separation processes have been reviewed several times [4–7]. Briefly, in an SLM system an organic solvent is immobilized in the pores of a porous polymer or inorganic support material by capillary forces, separating two aqueous solutions: the feed (donor) and the strip (receiving, acceptor) phase (Fig. 3.1). The compounds are separated from the aqueous sample feed phase into an organic solvent immobilized in a support diffusing through the membrane phase, and then they are continuously back extracted to the other side of the membrane into the

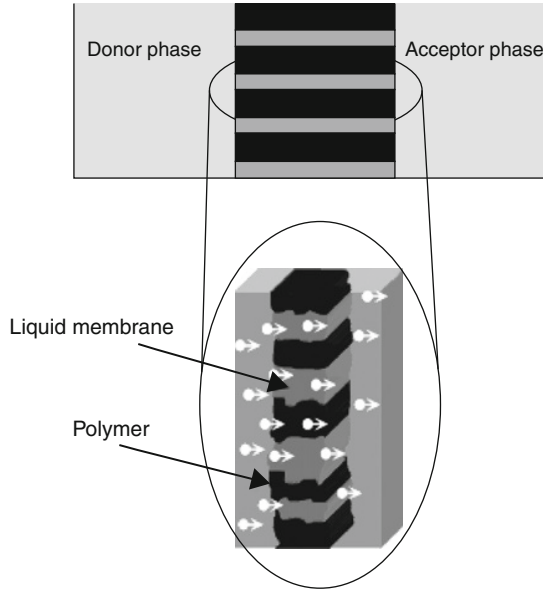

Figure 3.1 Scheme of a supported liquid membrane.

strip phase. The driving force is the difference in concentration of the compounds between the phases.

An SLM usually consists of an organic solvent immobilized in the pores of a hydrophobic microfiltration membrane. In many cases, the organic solvent contains a carrier which is able to selectively bind one of the components from the separated mixture (feed solution) which improves selectivity. The general term for mass transport through liquid membranes under the chemical potential gradient as a driving force is permeation. The permeants from liquid feed (donor solution) are transported through a nonporous, polymeric or liquid membrane phase and desorbed into another liquid phase. Schlosser [8] called this process pertraction, derived from the Latin "per-trahere," by analogy to the term extraction, which has been derived from the Latin "ex-trahere." The pertraction process can be seen as a combination of extraction and solvent stripping carried out simultaneously. While solvent extraction is an equilibrium process, pertraction is a dynamic, nonequilibrium diffusion process governed by the kinetics of the membrane transport. Therefore, the amount of transported compounds is not proportional to the amount of the organic, membrane phase as it is in extraction.

SLM separation systems can be classified into several different groups, according to their preparation methods, types of membrane support and membrane liquids, module types used and their application (for details, see Chapter 1).

Successful applications of SLMs are possible due to their advantages compared to other separation methods. The main advantages of SLMs are the small amounts of organic phase and extractant (carrier) used, one-step mass transfer, the possibility of achieving high separation factors, concentration of extracted compound(s) during separation, and low separation costs.

Nevertheless, there are some problems limiting the practical application of SLMs. The main problem is the stability of the liquid membrane, caused by leakage and/or losses of membrane phase components during transport process. However, by proper choice of the porous polymeric support, using organic solvents used as a membrane phase and membrane phase components, the instability can be significantly reduced.

3. Transport Mechanisms and Kinetics

The principal application of liquid membranes is to separate mixtures into their components and/or concentration (enrichment) of one or more of them. Such three-phase systems, when two miscible fluids are separated by a liquid which is immiscible with them, enable a mass transfer between these fluids. The efficiency of membrane transport for a particular compound

depends on its partition coefficient between the different parts of a membrane system. Only compounds, which are easily extracted from the feed (donor) phase into the membrane phase and easily re-extracted from the membrane to the strip (acceptor, receiving) phase, are transported. Therefore, the separation of different compounds is based on the same principle as a liquid extraction followed by a back extraction. Only molecules with different physicochemical properties can be separated, even if they are of equal size. Separation and concentration are an entropy decreasing, that is, free energy increasing, process and do not happen spontaneously. To run a continuous separation or concentration a source of free energy is needed. For this reason, it is necessary to establish the difference in the chemical potentials of the mixture components on opposite sides of the membrane. In the case of mixtures two important properties have to be taken into account, namely solubility and diffusion. Note that the solubility coefficient of a single component becomes more complex due to the presence of other substances in the mixture. Additionally, the diffusion coefficient of any substance in a mixture may be a function of the concentration of all substances present in the membrane. In such a case, more than one substance will be transported through the membrane and fluxes of different substances may interact and affect the separation process. Therefore, many mathematical models, like solution-diffusion or simple network models, as well as the numerical model [9], have been used to express the mass transfer through liquid membrane systems.

3.1. Driving force and transport mechanisms

As mentioned above, membrane transport is a dynamic, nonequilibrium process. The transported compound has to dissolve in the organic, hydrophobic membrane phase and diffuse through it to enter the aqueous stripping phase. The mass transfer in this system takes place due to the difference in the chemical potential across the membrane as a driving force. The variation of chemical potential of component i can be expressed as

$$\mathrm{d}\mu_i = RT\,\mathrm{d}\,\ln c_i + RT\,\mathrm{d}\,\ln \gamma_i, \tag{1}$$

where c_i is the concentration and γ_i is the activity coefficient.

The concentration profile in the SLM system is schematically shown in Fig. 3.2.

The transport of the substances from the feed solution to the strip side can be divided into the following steps: diffusion of substance S across the boundary aqueous layer in the feed (donor) phase, extraction (sorption) of substance on the donor/membrane phase interface, diffusion across the boundary layer on the feed (donor) side, convection transport in the liquid membrane zone, diffusion across the boundary layer on the strip (acceptor) phase of LM, re-extraction (desorption) on the membrane/strip phase

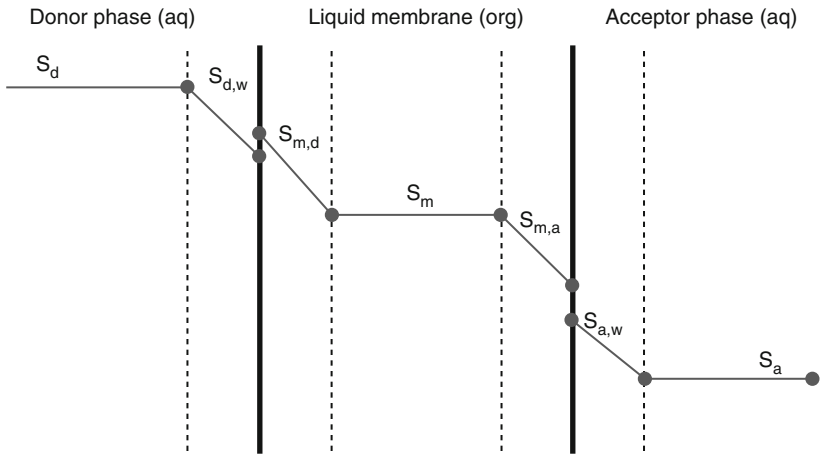

Figure 3.2 Concentration profile in SLM.

interface, and diffusion across the boundary layer in the strip (acceptor) phase.

The transport process itself is steady state, since the membrane surface area is small compared with the quantity of material to be transported and in the case where the activity coefficient is close to one the overall membrane flux (J) can be derived by applying Fick's first law:

$$J = k_{\mathrm{m}} \Delta C / d. \tag{2}$$

Here, k_{m} is the mass-transfer coefficient and is proportional to $K_{\mathrm{m}} D_{\mathrm{m}}$, where K_{m} is the partition coefficient and D_{m} is the diffusion coefficient. ΔC is the concentration difference between the strip and feed phases and d is the membrane thickness.

The membrane phase diffusion coefficient D_{m} for bulk liquid membrane is equal to the diffusion coefficient in bulk solution D_0. The diffusion coefficient is an important factor in the transport mechanism and is related to the viscosity by the empirical Stokes-Einstein equation [10]:

$$D_{\mathrm{m}} = D_{\mathrm{o}} = kT/(6\pi\eta r) \tag{3}$$

or

$$P = kTK_{\mathrm{f}}/(6\pi\eta r_{\mathrm{s}} d), \tag{4}$$

where D is the solute diffusion coefficient (cm^2/s), k is the Boltzmann constant, T is the absolute temperature in Kelvin, η is the viscosity of the organic phase (solvent), and r_{s} is the molecular radius of the solute (cm). P is the permeability of the solute (cm/s), d is the thickness of the membrane (cm), and K_{f} is the partition coefficient of the solute between the organic

(membrane) phase and the water (feed) phase. The diffusion of solvents immobilized in membrane pores is much slower than in bulk solution [11].

For an SLM, the flux can be given by the equation:

$$J = D_{\mathrm{SLM}} K_{\mathrm{f}} \Delta C / d. \tag{5}$$

The D_{SLM} is the SLM diffusion coefficient and K_{f} is the distribution (partition) coefficient.

In an SLM, the effective diffusion coefficient has to be corrected according to the morphological characteristic of the porous polymeric membrane in which the liquid is immobilized. Therefore, the apparent diffusion coefficient D_{SLM} is related to the coefficient in bulk membrane phase D_{m}, through [12]

$$D_{\mathrm{SLM}} = D_{\mathrm{m}} \varepsilon / \tau, \tag{6}$$

where ε is the membrane porosity and τ is the tortuosity, related to the tortuosity factor β, defined as the average pore length/membrane thickness.

The separated substances can be transported across the membrane according to two main classes of transport mechanisms: simple permeation (passive diffusion) and carrier-mediated transport. Their occurrence significantly depends on the type and properties of transported compounds.

3.1.1. Simple permeation

In this transport mechanism, the transported substance dissolves in the organic membrane phase and diffuses to the receiving phase due to the concentration gradient between these two phases.

In simple pertraction (Fig. 3.3A), the permeant passes through the membrane due to its solubility in the organic phase. The transported compound is in the same form in both feed and strip phases, and the transport (permeation) stops when equilibrium concentration is reached, and it is impossible to concentrate the transported compound. As an example of this type of process, the separation of aliphatic from aromatic hydrocarbons can be given [8]. The transported molecules have to be uncharged in the feed phase for extraction to the hydrophobic membrane phase.

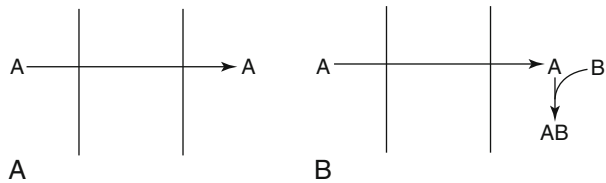

Figure 3.3 Transport mechanism: (A) simple pertraction and (B) pertraction with reaction in stripping phase.

The selectivity of separation and/or the pertraction capacity can be increased if the permeant undergoes a chemical reaction in the stripping phase. The separation effectiveness is significantly improved if the component to be removed is transformed almost quantitatively into an impermeable form in the receiving phase. Therefore, the product is insoluble in the membrane phase, which prevents it from diffusing back through the membrane (Fig. 3.3B). In this way, the concentration gradient can be maintained across the membrane, hence facilitating solute enrichment. Also, selectivity can be further enhanced by proper choice of the reaction window in the stripping solution, so that only the compounds of interest are ionized and trapped.

3.1.2. Carrier-mediated (facilitated) transport

Pertraction with SLMs utilizes as its principle of separation the high diffusion coefficient of solutes in liquids and the very high and different solubility of pertracted compounds in some liquids. When this solubility is too low, effective and selective transport is difficult to achieve, even if the trapping in the strip phase can be easily done. When there are various nontransportable, permanently charged compounds (with low solubility in the liquid membrane phase) such as metal ions, amino acids, or peptides, a chelating agent or carrier can be added to the membrane phase. The permeability and selectivity of SLM transport can then be increased by several orders of magnitude. The carrier should reversibly react with the pertracting compound and form a complex which can be transported through the organic membrane phase. In this situation, it is important that the carrier and its complex formed with the transported compound are soluble in the membrane but not in the feed and strip aqueous phases. Carrier-mediated transport can be limited by complexation reaction kinetics or by diffusion of the complex through the membrane phase. In many reports, the facilitated transport mechanism is analyzed using a complicated expression with membrane diffusion and a chemical reaction [13–16]. Facilitated transport through an SLM is usually described based on the idea that the reaction between compounds with the carrier takes place only at the membrane surface, a feed solution-liquid membrane interface. Such a simple mechanism in which the carrier stays in the membrane and two ion-exchange reactions take place on the water/membrane interfaces is called "Small Carrousel" [17]. Nevertheless, if the carrier is not very hydrophobic, it can leave the membrane interior and the chemical reaction takes place mainly in the aqueous phase. The mechanism in which the carrier moves from one aqueous phase through the membrane into another before returning and completing the cycle is called "Big Carrousel" [18]. When the ligand (L_m) is located in the membrane phase and is able to form a complex (SL_m) with the substrate (S_m), such reaction takes place in the membrane phase, characterized by the dissociation constant (K_a):

$$S_m + L_m \leftrightarrow SL_m, \tag{7}$$

$$K_a = [SL_m]/[S_m][L_m]. \tag{8}$$

If the association and dissociation processes are fast the transport is limited by diffusion and the flux decreases linearly with increasing the membrane thickness. Therefore, the flux can also be expressed using Fick's first law:

$$J = D_{CS}\Delta C_{CS,m}/d \tag{9}$$

and

$$\Delta C_{CS,m} = C_{S,0}K_{ext}, \tag{10}$$

where $\Delta C_{CS,m}$ is the concentration gradient of the carrier-substance complex, $C_{S,0}$ is the initial concentration of transported substance, and K_{ext} is the extraction constant and can be written as

$$K_{ext} = K_f K_a. \tag{11}$$

The possibility of using various compounds as a carrier resulted in different versions of the carrier-mediated transport mechanism such as simple carrier permeation in the strip phase, coupled cotransport, and coupled countertransport (Fig. 3.4).

In simple carrier permeation transport, the carrier reversibly reacts with extracted compound in the feed phase or at the feed-membrane interface, and forms an extractable complex. This complex is transported through the membrane phase in a similar way as in simple permeation without using a

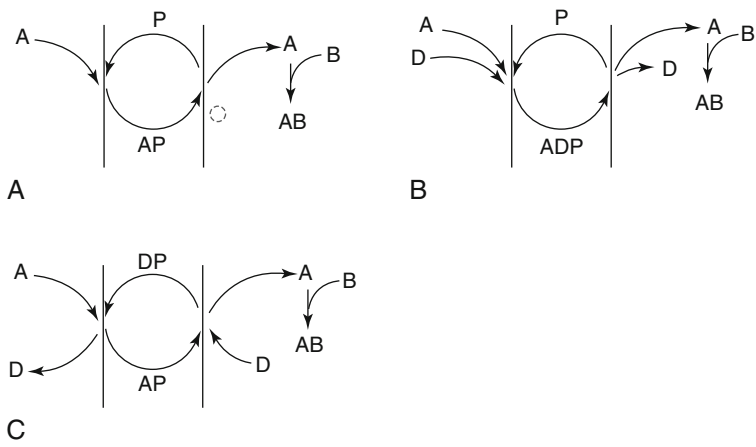

Figure 3.4 Carrier-mediated transport mechanism: (A) simple, (B) cotransport, and (C) countertransport.

carrier. At the membrane-strip phase interface, the compound can be trapped by another ligand used in the strip phase which forms a stronger and, in many cases, charged complex (Fig. 3.4A). Therefore, a permanent concentration difference is present through the membrane during the extraction time and a high enrichment factor can be achieved. For example, anionic surfactants can be transported by an ammonium compound [19] and the metal ions or organic acids by a variety of complexing agents [20].

In coupled transport, the complexation reaction between the carrier and extracted compounds takes place only at the water-membrane interface. The complex is formed at the feed-membrane interface and is transported through the membrane to the membrane-strip phase interface. An additional compound is transported together with this complex, in the same or opposite direction. At the membrane-strip phase interface, the decomposition of the complex takes place. In this type of transport, two substances are transported and at least two mass fluxes are realized. If both fluxes are in the same direction, coupled cotransport can be distinguished. If mass fluxes are in the opposite direction, a coupled countertransport occurs. Thus, the flux magnitude depends on the type and concentration of the carrier and transported substances.

When the carrier used in the membrane phase is in an uncharged form, the transported ionic substance can be extracted only as an ion pair, which is formed by adding to the feed phase a counterion or chelating agent. The carrier reacts with such a neutral ion pair giving a complex which is transported through the membrane (Fig. 3.4B). The concentration gradient of cotransported compound is the driving force in this type of transport. The uranyl sulfate anions transport by a tertiary amine carrier is an example of such coupled cotransport [21]. Transport of amino acids [22, 23] and peptide hydrochloride [24] by macrocyclic carriers is another example of cotransport involving ion-pair interaction with a neutral carrier. Thus, ionic substances and their counterions are transported in the same directions and their fluxes are stoichiometrically coupled.

Many permanently charged compounds, especially amino acids and their derivatives, can also be efficiently transported through liquid membranes by ionic carriers. In these cases, a gradient of counterions from the strip (receiving) phase to the feed (source) phase provides the driving force for the transport. Therefore, the amino acid carrier complex is transported through the membrane from the feed to the strip phase, and the counterions are transported in the opposite direction, that is, coupled countertransport (Fig. 3.4C). For transport of amino acids using Aliquat 336 as a carrier, a gradient of chloride ions from the strip to the feed phase provides a driving force for the mass transport [25]. Using DEHPA as a carrier for amino acid permeation, a pH gradient is created over the membrane [26]. The strip phase is kept strongly acidic ($pH \leq 1$) while $pH \approx 3$ for the feed phase.

3.2. Product recovery and enrichment

The quantitative and selective recovery of any substance is very important in a separation process. Parameters which are usually used for the description of membrane processes are pertraction efficiency and/or recovery. Additionally, especially in analytical applications, the enrichment factor is crucial.

As presented in the previous equations, the rate of mass transfer, and thus the pertraction efficiency, is proportional to the concentration difference ΔC over the membrane and can be expressed:

$$\Delta C = \alpha_f C_f - \alpha_s C_s K_s / K_f, \tag{12}$$

where α_f and α_s are the fractions of the transported substance, which is pertractable from the feed to the strip phases, respectively. C_f is the total concentration in the feed phase, while C_s is the total concentration in the strip phase. K_s is the partition coefficient for the substances between the strip and membrane phase, and K_f is the partition coefficient for the substances between the feed and membrane phase. While the feed and strip phases are mostly aqueous, both partition coefficients are similar. However, in some cases, the different ionic strengths of feed and strip phases can cause significant differences between K_s and K_f. Then, the concentration difference can be expressed as

$$\Delta C = \alpha_f C_f - \alpha_s C_s. \tag{13}$$

Usually, the membrane separation conditions are set to get α_f close to unity and α_s a very small value. The value C_s is zero from the beginning of the pertraction and increases successively to equilibrium, when concentration in the strip phase is the same as in the feed phase. The maximum concentration-enrichment factor (E_e) is obtained when ΔC has eventually reached zero:

$$E_{e(max)} = (C_s / C_f)_{max} = \alpha_f / \alpha_s. \tag{14}$$

The rate at which this condition is approached depends on many parameters, like diffusion coefficients in feed and membrane phases, partition coefficients, or membrane thickness. We can have two situations: membrane-controlled pertraction, when the diffusion of the transported compound through the liquid membrane is the limiting step, and feed-controlled pertraction, when the diffusion through the feed phase to the feed-membrane interface is the limiting step [27].

The pertraction efficiency, E, is defined as the fraction of substances transported from the feed (donor) phase to the strip (acceptor) phase. It is the measure of the rate of mass transfer through the membrane and is constant at specified pertraction time, phase composition, and ionic strength. The pertraction is expressed as

$$E = n_s / n_f = (C_s V_s) / (C_f V_f) \tag{15}$$

or

$$E_w = n_f - n_w/n_f, \tag{16}$$

where E_w is the pertraction efficiency; n_f, n_s, and n_w are the total amounts of pertracted compound in the feed, strip, and waste (outflux of the continuously pumped feed phase after contact with the membrane phase) phases, respectively. V_s and V_f are the volumes of the strip and feed phases. The value of E indicates how much of the compound is found in the strip phase, and E_w indicates how much of it is removed from the feed into the organic membrane phase. Thus, we can define the recovery R, as

$$R = E/E_w. \tag{17}$$

If E is equal to E_w, no substance is lost during the process and recovery is 100%, but if E is smaller than E_w some part of the pertracted compound is either adsorbed in the apparatus or left in the membrane phase. The latter effect can limit the SLM pertraction in some cases. In practice, the problem can be overcome by careful design of the experimental conditions.

4. Selectivity

The selectivity of the membrane process is the ability to transfer the compounds of interest but not the interfering compounds. The selectivity depends mostly on the membrane transport mechanisms and trapping method used. In simple permeation, the selectivity is not high and is governed by solubility differences between the sample components in the membrane phase. The pertraction efficiency and selectivity can be increased by adding specific carrier to the membrane phase.

The selectivity can be greatly enhanced by using specific antibody-antigen (Ab-Ag) interactions in the transport mechanism. Two main groups, mono- and polyclonal antibodies, can be used for selective liquid membrane pertraction of different compounds.

Another important problem is the enantiopurity of chiral pharmaceuticals and many other compounds with biological activity. Therefore, there is a great interest in developing methods that can help in stereoisomer separation and improve the stereoselectivity of separation methods. In this case, a specific chiral environment should be created to ensure enantioselectivity of separation.

4.1. Transport selectivity

The transport selectivity in the membrane pertraction process depends on the type of transport mechanism.

4.1.1. Selectivity of the simple permeation process

In simple permeation transport, the selectivity is not high and is governed by solubility differences between the sample components in the membrane phase. While the diffusion coefficient depends on the molecular radius of the solute, it could also affect the selectivity. The selectivity can be increased when the compounds are in different forms, active in the feed phase and inactive—by changing the pH or a specific reaction—in the strip phase. In this way, selective transport of acids and bases, for example, amines, can be achieved. The simplest way to improve selectivity and mass transfer is to adjust the pH of the aqueous phase, for example, the basic feed phase and acidic strip phase for selective amines extraction. If the pH of the feed (donor) phase is adjusted to a sufficiently high value, the transported amines are uncharged and are transported over the organic liquid that is used as a membrane phase. The strip (acceptor) phase on the other side of the membrane is an acidic solution or buffer with low pH. An amine molecule that diffuses through the membrane is immediately protonated at the membrane-strip interface, and is thus prevented from re-entering the membrane. The principle of SLM pertraction of basic compounds, for example, amines, is shown in Fig. 3.5.

It is clear that acidic compounds will be already charged (dissociated) in the alkaline feed solution and consequently not transported. Neutral components may be transported, but will distribute freely between all three phases. Macromolecules such as proteins will typically be charged, and therefore not transported. The pertraction rate of uncharged macromolecules will be very low, owing to their high radius and thus low diffusion coefficient. In summary, in the mentioned conditions, the SLM pertraction will be highly selective for small, basic compounds. The selectivity can be further tuned by careful selection of pH of the feed and strip phases. For example, it has been possible to discriminate aromatic amines, whose pK_a are around 5, and aliphatic amines with pH equal to or higher than 10.

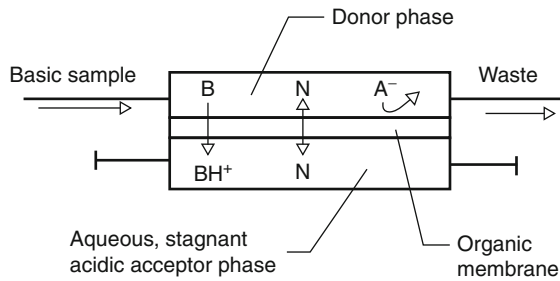

Figure 3.5 Schematic description of the SLM principle. From Ref. [27] with permission. © 2008 Elsevier.

Acidic compounds may be pertracted in a similar way to amines, but by reversing the pH conditions, acidic feed phase and basic strip phase.

Usually, nonpolar organic liquids are used as a membrane phase; therefore, polar compounds are less efficiently pertracted than hydrophobic ones. It is possible to increase the selectivity by making the liquids more polar or by adding ion-pairing or chelating reagents to the feed phase. One example of reagents added to the feed phase for metal ions pertraction is 8-hydroxyquinoline, which forms transportable complexes with many metals [20]. This complex is transferred through the membrane and the metal ions are trapped in the strip phase by another ligand, DTPA (diethylenetriaminepentaacetic acid), forming a stronger and nonpertractable charged complex.

4.1.2. Selectivity of carrier-mediated transport

The pertraction efficiency and selectivity can also be increased by adding specific carrier to the membrane phase. Various carrier molecules or ions can be incorporated in the membrane phase to enhance the selectivity and mass transfer. Most carriers used for this were originally developed for solvent extraction [28]. However, many new carriers were designed only for liquid membrane pertraction. Characteristic features of a good carrier for SLM pertraction are:

- Rapid kinetics of formation and decomposition of the complex on membrane interfaces
- No side reactions
- No irreversible or degradation reaction
- No copertraction of solvent
- Low solubility in the aqueous feed and strip phases
- Low toxicity to biomass, especially in the case of application in biological systems
- Acceptable price, especially in industrial applications

Taking into account the characteristics of a good carrier as listed above, various different carrier molecules or ions can be incorporated in the membrane phase to enhance selectivity. Many macrocyclic multidentate ligands such as crown ethers and kryptands are used (Fig. 3.6). Crown ethers and other macrocyclic compounds have a pronounced selectivity for metals [11, 29] and for amino acids and peptides [23].

TOPO (trioctylphosphine oxide), a compound that forms hydrogen bonds, is also used for carboxylic acids pertraction (Fig. 3.7). The pertraction efficiency of carboxylic acids of different polarities is strongly influenced by the content of the carrier in the membrane [30].

As the ionic carriers, mostly amines or carboxylic and phosphoric acids (Fig. 3.7) for metals, organic acids, and amines are typically used. A common carrier that has been used is Aliquat 336, a quaternary ammonium ion,

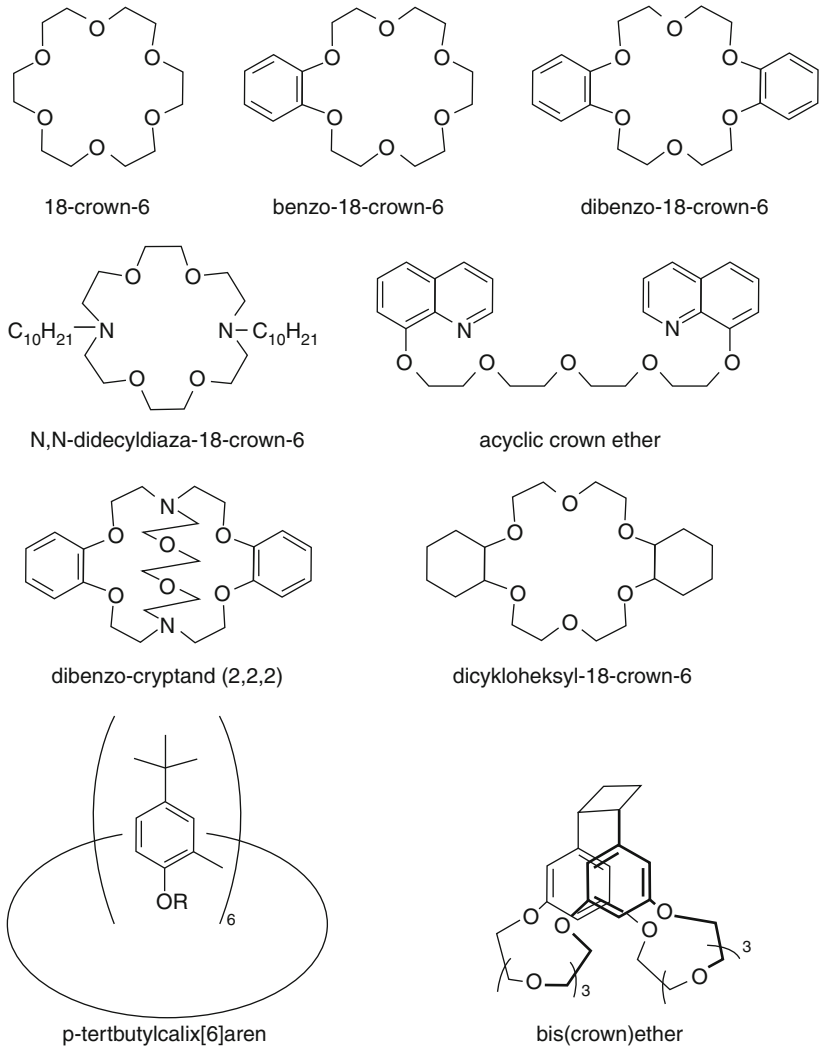

Figure 3.6 Macrocyclic carriers.

permanently positively charged in an ion pair with chloride. For metal extraction, the addition of thiocyanate ions to the donor is needed to form a negatively charged metal-thiocyanate complex, which can give an ion pair with the carrier [20]. Organic acids and amino acids are effectively transported with Aliquat 336 from basic solutions, where they are negatively charged [25]. Components that are not negatively charged in these conditions and cannot give an ion pair with cationic carrier are not extracted. The selectivity of organic and amino acids can be increased by carefully adjusting

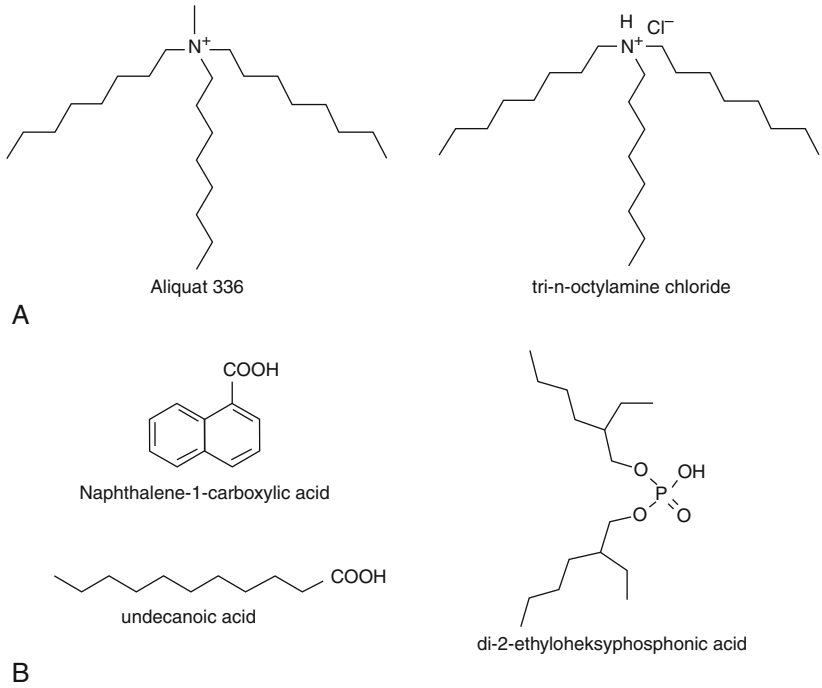

Figure 3.7 Ionic carriers: (A) cationic and (B) anionic.

the pH of the feed phase. The pK_a of transported compounds must differ by at least 2-3 orders of magnitude.

This ion-pair strategy was also used for transport of anionic surfactants with sulfuric acid anions, which cannot be protonated as carboxylic acids, and therefore not be transported by simple permeation [19]. SLM with Aliquat 336 as a carrier and chlorine ions gradient as a driving force was used for pertraction of glyphosate [*N*-(phosphonomethyl)glycine], a herbicide widely used all over the world, and its main metabolite, (aminomethyl) phosphonic acid (AMPA). The results show that it is possible to transport both glyphosate and AMPA in one step by adjusting the pH of the feed phase to higher than 10. When the pH of the feed phase is lower than 7, glyphosate could be transported selectively [31, 32].

There are a number of organic acids used as ionic carriers for metal ions and amines or amino acids pertraction. The mostly used anionic carrier for metal ions and amino acids is di-2-ethylhexyl phosphoric acid. The carrier is dissolved in the membrane phase as a dimmer, which reacts at the donor phase-membrane interface with amino acid cation, forming an ion pair and releasing a proton. For example, selective speciation of different chromium species (chromate and chromium ions) was achieved by the combination of

two pertraction systems, one working with DEHPA for Cr^{3+} transport and the other with Aliquat 336 for chromate anions [33].

However, various carrier molecules or ions have been used in the membrane phase and many reagents in the strip phase for trapping, to enhance selectivity and mass transfer the pertraction, are often not selective enough. Such selective extraction could be obtained by utilizing soluble antibodies in the strip phase.

4.2. Immunological trapping

Selectivity can be greatly enhanced by using specific antibody-antigen (Ab-Ag) interactions in the pertraction mechanism. This mechanism was first used for the trace-level determination of pollutants in complex environmental matrices, using selective solid-phase extraction with immunosorbent as an extraction step. Antibodies can be immobilized on a solid support, for example, silica beads, to yield selective phases, called immunosorbents. These have been used for the extraction of many different compounds from various environmental matrices [34]. Exploring antibodies as specific reagents in liquid membrane pertractions promises a high degree of selectivity and enrichment. Utilizing membranes for matrix cleanup and antibodies for selective recognition is a powerful combination for selective pertraction. This extends the scope of SLM to include permanently neutral compounds that have not been feasible to enrich in standard SLM systems. A specific, for transported compounds, antibody (Ab) is introduced as trapping reagent into the SLM strip (acceptor) phase. If there are permanently neutral compounds in the feed (donor) phase, or the pH is adjusted so that the compounds (Ag) are uncharged, they are extractable into the organic membrane phase. After pertraction the uncharged compound diffuses through the membrane phase to the membrane-strip phase interface where it is re-extracted down the concentration gradient. The gradient is upheld by the binding of the transported compound (antigen, Ag) to the compound-specific antibody forming a nonpertractable antibody-antigen (Ab-Ag) complex in the strip phase. Thus antibody-antigen complex formation is the heart of the pertraction system.

Good trapping capacity is obtained because of the high affinity of the antigen toward its antibody. The schematic immuno-SLM pertraction system is shown in Fig. 3.8.

Immuno-SLM system was successfully applied as a sample preparation method for 4-nitrophenol and atrazine detection in water and juice samples. Polyclonal anti-4-nitrophenol antibodies were used for SLM immunopertraction from spiked reagent and wastewater samples [35]. The immuno-SLM was also used for selective pertraction of the popular herbicide atrazine as a model sample from tap and river water samples as well as from orange juice [36].

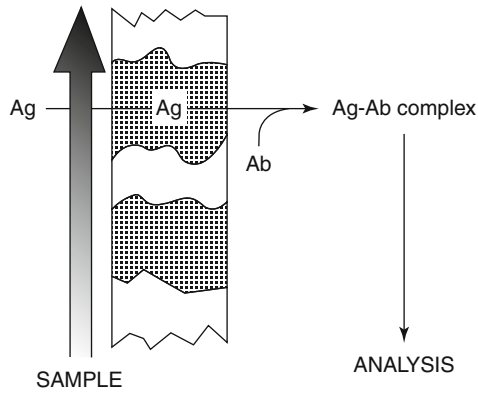

Figure 3.8 Immuno-SLM scheme.

4.3. Stereoselectivity

Almost all newly designed and biologically active substances, such as drugs or pesticides, are compounds with a strictly defined stereostructure. Therefore, there is a great interest in obtaining compounds with the required enantiopurity. This can be achieved by different approaches including stereoselective synthesis, biotransformation, or chiral separation. There is great pressure to develop methods that can help in the separation of stereoisomers. Different types of membrane processes, also involving SLM transport, have been applied for the separation of stereoisomers. Moreover, SLMs are sometimes additionally utilized as a convenient tool to examine the nature of stereoselective interaction with chiral carriers. To assure the transport stereoselectivity, and possible resolution of enantiomers, a chiral environment is required in the system. In SLMs, it can be achieved in two manners, namely by an application of a chiral organic liquid as a membrane phase and by introducing a chiral carrier into an achiral membrane [37].

The use of chiral membrane solvent to achieve transport stereoselectivity is not very widespread. Probably, the only report describing chiral liquid-phase-enhanced stereoselective transport is amino acid enantiomers separation by means of chiral alcohols, nopol and (2S)-(−)-methylbutan-1-ol [38] (see Fig. 3.9). It was shown that optical separation of six pairs of enantiomers of amino acids is possible in this way. However, the chiral discrimination (expressed as a flux ratio for both enantiomers and denoted as α) was moderate and the best result was 1.27 for serine. As a main conclusion, it was stated that the factor involved in chiral discrimination was an asymmetry of the amino acid molecule.

The most extensively examined method of stereoselective SLM separation is carrier-facilitated transport with chiral carriers. Different macrocyclic compounds, transition metal complexes, phosphates, lariat ethers, podands,

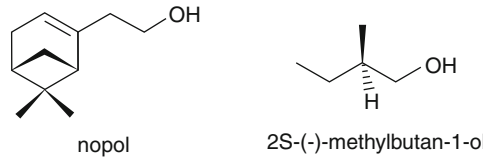

Figure 3.9 Chiral solvents.

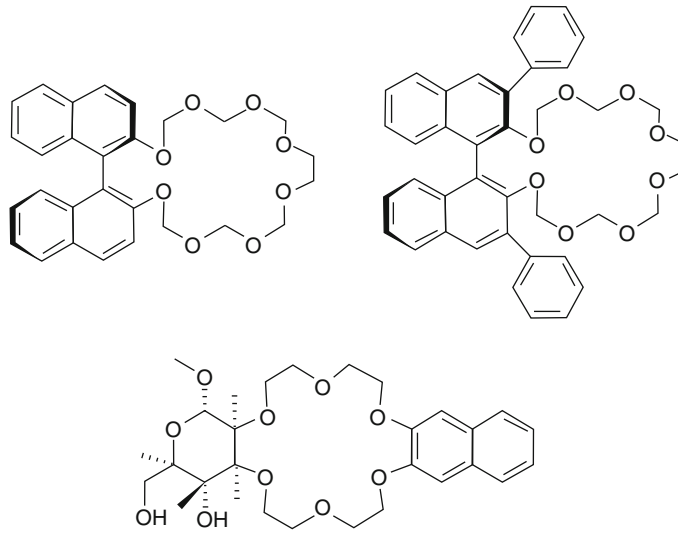

Figure 3.10 Selected macrocyclic chiral carriers.

amino acid derivatives, and macrocyclic pseudopeptides were examined as chiral carriers in liquid membranes (for selected examples, see Figs 3.10–3.12). Chiral crown ethers with naphthalene rings were applied as carriers for amino acid enantiomers transport with good selectivity, depending on the carrier and amino acid structure [39]. The other similar type carriers, optically active D-mannose derivatives of crown ethers, were examined in enantiomer separation of aromatic amino acids, in bulk and supported liquid membranes. By application of such carriers, a high separation factor of amino acid can be observed [40].

An interesting group of chiral carriers are those formed by species that utilize interactions between transported enantiomer and transition metal complexes. For instance, such a compound, acting as an additional chiral ligand for the copper central cation, is able to recognize an amino acid Cu(II) complex present in the feed phase. This double chiral carrier-amino acid-Cu (II) complex becomes diastereoisomeric and can be transported through a

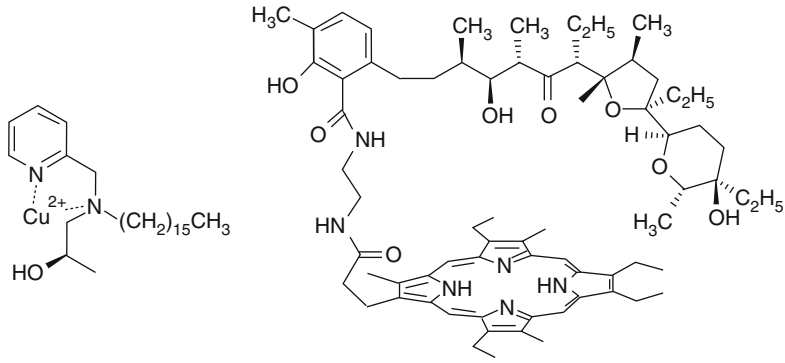

Figure 3.11 Hydrophobic Cu-chiral ligand complex and sapphyrin-lasalocid chiral conjugate carriers.

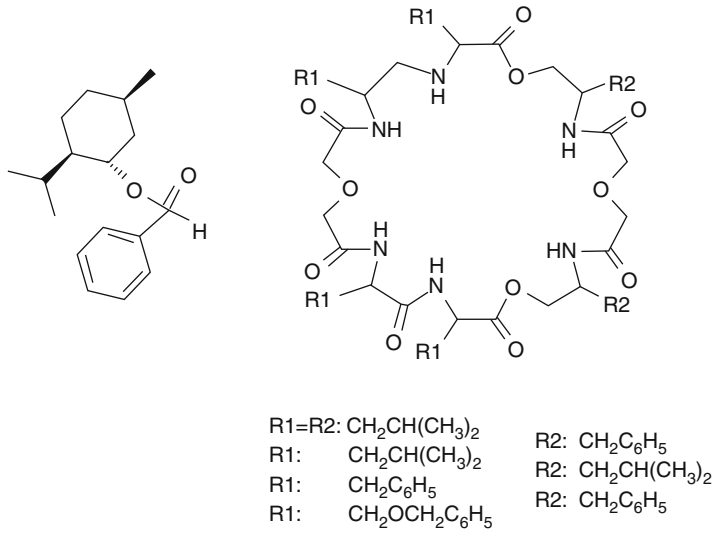

Figure 3.12 Chiral phosphoric acid derivative and macrocyclic pseudopeptide carriers.

liquid membrane in a cotransport and by this way both optical isomers are differentiated [41]. The other example of a structurally complicated chiral carrier is sapphyrin-lasalocid conjugate. It was applied in zwitterionic amino acid enantiomer separation in countercurrent transport, but only modest stereoselectivity, ranging between 1.5 and 2.0, was obtained [42].

Other classes of substances tested as potential chiral carriers in SLMs are dialkyl and monoalkyl phosphates, phosphonates, and phosphinates based on (−)-menthol and (−)-nopol [43]. The amino acids are transported

through the membrane according to the countertransport mechanism and, in this case, the alcohol and aromatic carrier moieties are responsible for chiral interactions. The obtained fluxes were quite high, but the enantioselectivity was moderate. Chiral *N*-blocked amino acid derivatives and macrocyclic pseudopeptides are very interesting carriers for amino acid esters and salts separation [44, 45]. It was shown that they can act as effective transporters and chiral selectors for amino acid methyl esters. The selectivity obtained is moderate, however, and depends on the type of applied carrier and ester structure.

An interesting example taking the opposite approach was presented by Wieczorek *et al.* [24]. To separate a mixture of dipeptide diastereoisomers and their phosphonic analogues, achiral crown ethers were used as transport enhancers. In this case, the diastereomeric complex is formed between the chiral transported molecule and not the optically active carrier. The observed stereoselectivity depends on the peptide structure and was independent of the presence of carrier, but the application of carrier increased the transport rate of both diastereoisomers.

It can be concluded that stereoselective (and particularly enantioselective) separation can proceed by the simple application of a chiral organic phase or in most cases by incorporation of carriers in the membrane phase. Sometimes, their structure is very complex and these molecules can act as ''real'' receptors for the enantiomers. Different types of transport mechanisms are involved in the separation and the most popular one is cotransport. This is a result of the fact that most frequently used carriers are based on crown ethers' structure. The stereoselectivities by application of carrier-mediated SLM separation are very different and depend on the structure of the guest and host molecules. The magnitudes of the stereoselectivity are in most cases moderate but similar to other membrane-based separation techniques for stereoisomers.

5. Process and Membrane Units Design

5.1. Commonly used supports

In the SLM process, like in all membrane processes, the membrane plays a key role in the transport and separation efficiency. The permeation rate and separation efficiency depends strongly on the type of liquids and supports used for SLM construction. However, the transport properties depend on the type of liquids used as a membrane phase; the liquid membrane stability and mechanical stability depend, to a large extent, on the microstructure like pore shape, size, and tortuosity of the membrane used as a support. Therefore, many types of polymeric and inorganic microporous membrane supports are studied for the liquid membrane phase immobilization.

5.1.1. Polymeric support

Since the development of asymmetric synthetic polymer membranes, a number of membrane applications have been achieved. Most industrial polymers have been applied for nonporous and porous membrane formation. For immobilization of the liquid membrane phase, the microporous polymeric membranes are usually used and they are an integral part of the SLM manifold. In most cases, the choice of the polymeric support has an influence on the SLM stability, lifetime, and performance of the liquid membrane. It is thus very important to select a particular support for a given liquid membrane phase. The polymeric support should be characterized by high hydrophobicity, high porosity, small pore size, and proper tortuosity. The most important factors that influence the SLM system performance are physical stability of the support and the rate of the mass transfer through the membrane (flux of the solute). As a consequence, the support should be as thin as possible to maintain high fluxes, which depend on the diffusion pathway. However, thin supports are mechanically unstable. Often asymmetric porous membranes are used, for example, Fluoropore FG in which one microporous membrane (e.g., PTFE) is used for immobilization of organic phase and the second, thicker porous membrane is used to enhance the durability against physical stress. The character of the polymeric support also influences the liquid membrane stability; this issue will be presented below. As a polymeric support in flat sheet or hollow-fiber membrane configurations, polymers such as polypropylene (PP), polyethylene (PE), and poly(tetrafluoroethylene) (PTFE) are most frequently used. In Tables 3.1 and 3.2, characteristics of the commercially available microporous supports are presented together with the producer name.

5.1.2. Inorganic support

Although the design of new polymers for membrane formation is still in progress, the utilization of advanced inorganic membrane materials, such as ceramics, metals, porous metal oxides, and zeolites, is nowadays very important. The general advantages of inorganic membranes are mechanical and thermal stability, solvent and chemical resistance, sterilization ability, and biocompatibility. The progress in solid-state science allows preparation of new inorganic membrane materials. Sol-gel processing, plasma-enhanced chemical vapor deposition and hydrothermal synthesis are used for inorganic membrane formation. These membranes, as well as organic-inorganic composite membranes, are used in many processes, especially in nanofiltration, pervaporation, gas separation and catalytic membrane reactors [46–48]. Such membranes as well as hybrid organic-inorganic membranes have been successfully used for facilitated transport of solutes in liquid media. Hybrid membranes, prepared by incorporation of cellulose triacetate plasticized membranes with Aliquat 336 as a carrier, on inorganic silanes material prepared by sol-gel method, were used for platinum group ions transport. The results show that these membranes present higher selectivity toward

Table 3.1 Characteristic of some commercially available membranes used as a polymeric support in flat-sheet supported liquid membranes (FS-SLM)

Commercial name	Material	Producer	Thickness (μm)	Porosity (%)	Pore size (μm)
Celgard 2400	PP	Celanese	25	38	0.02
Celgard 2500	PP	Celanese	25	45	0.04
Accurel	PP	Enka	100	64	0.10
Accurel	PP	Enka	150	70	0.20 or 0.40
Accurel	PP	Enka	160	75	0.20
Accurel 1E-PP	PP	Enka	75	73	0.10-0.30
Accurel BS7C	PP	Armak	50	48	-
Duragard 2500	PP	Polyplastics	25	45	0.04
FP-DCH	PTFE	Flow Lab.	150	80	0.45
FHLP	PTFE	Millipore	60	85	0.50
FP-045	PTFE	Sumimoto	80	73	0.45
Millipore	PTFE	Millipore	125	68	10
Goretex	PTFE	Gore	60	78	0.20
Fluoropore FG	PTFE/PE	Millipore	60/115	70	0.20
Fluoropore FP-200	PTFE	Millipore	100	83	2.0
Fluoropore FP-045	PTFE	Millipore	80	75	0.45
Fluoropore FP-010	PTFE	Millipore	60	55	0.10
Nucelopore	Polycarbonate	Nucelopore Corp.	10	12	0.40

Table 3.2 Hollow-fiber polymeric membranes typically used as supports for SLM

Hollow fiber	Material	Producer	Inner diameter (mm)	Thickness (μm)	Porosity (%)	Pore size (μm)
Goretex TA001	PTFE	Gore	1.00	400	50	2
Trial manufacture	PE	Ashai Kasei	280	0.05	-	-
KPF-190M	PP	Mitzubishi Rayon	0.20	22	45	0.16
EHF-207T	PE	Mitzubishi Rayon	0.27	55	70	0.27

Pt(IV) than Pd(II) [49]. An interesting system, with asymmetric inorganic membranes, was used for selective metal ion separation. The membrane phase was a self-assembled monolayer of alkyl thiols as a hydrophobic phase for a trialkyl phosphate and phosphine oxide-based metal ion carrier. This organic mixture was attached on alumina porous supports with thin layers of gold. The thin membrane layer gave high fluxes and high selectivity, while metal ions transport was carrier limited [50].

Catalytically active supported ionic liquid membranes were used for propylene/propane vapor mixture separation. In this case, the ionic liquid was immobilized in the pores of an asymmetric ceramic support, displaying sufficient permeability, good selectivity, and long-term stability [51]. Porous inorganic membranes were also used as a support for chiral-selective liquid membranes. For this purpose, porous tubular ceramic membranes were impregnated with β-cyclodextrin polymer. Such SLMs were used for separation of enantiomers of racemic pharmaceutical chlorthalidone [52].

Although the inorganic supports show many advantages such as temperature stability, solvent, and mechanical resistance, there are not many papers dealing with the use of these membranes for SLM construction, probably due to the same problems as for polymeric supports: membrane stability and lifetime.

5.2. Organic solvents used in SLM

In making the choice for an organic liquid membrane solvent, several aspects should be taken into consideration. First of all, the organic liquid should be hydrophobic enough to ensure immiscibility with aqueous phases. Secondly, the solvent has to be characterized by low viscosity, which results in high mass transfer through the membrane. In this case, note that low viscosity decreases membrane stability. Surface tension

between the organic phase and polymeric support is also essential due to the fact that the liquid membrane is kept in the support pores by capillary forces. The other important factor is solvent volatility (mostly depending on the solvent density), which should be low to keep the organic phase in the pores of the support. Also, interfacial tension and the surface contact angle between the aqueous and organic phase has to be considered. The low interfacial tension causes faster degradation of the liquid membrane, for example, by easier emulsion formation, but on the other hand it increases the mass transfer by facilitating contact between phases. It is important for the carrier-mediated transport that organic solvent easily solubilizes the carrier. The magnitude of the fluxes in this type of transport depends on the carrier concentration. The high solubility of the carrier causes the high mass transfer. For these reasons, the most commonly used organic solvents as the liquid membrane phase are hydrocarbons (aliphatic and aromatic), hydrophobic ethers and esters, long-chain alcohols, or mixtures of technical solvents, for example, kerosene (Table 3.3). Concluding it is not straightforward to select an organic solvent and the choice is a compromise among all the discussed properties and also the type of support.

5.3. Ionic liquids as membrane phase

A new approach in the use of organic solvents for preparation of SLMs is the application of ionic liquids. ILs are compounds composed of two parts: cationic organic moieties and an anionic, organic, or inorganic part. The cationic parts of most ionic liquids are organic based, including imidazolium,

Table 3.3 The selected properties of the commonly used organic solvents as a membrane phase

Organic solvent	Density $\times 10^3$ (kg/m^3)	Viscosity $\times 10^3$ (Pa s)	Surface tension $\times 10^3$ (N/m)	Solubility in water $\times 10^{-3}$ (kg/m^3)
Di-*n*-butyl phthalate	1.04	15.4	36.4	8.91
n-Amyl benzoate	0.95	3.42	32.7	8.06
Dodecane	0.75	1.50	24.9	0.07
Heptane	0.68	0.38	19.6	-
Toluene	0.87	0.54	27.9	-
Kerosene	0.79	1.24	25.3	-
o-Nitrophenyloctylether	1.04	12.5	33.9	0.16
Diphenyl methane	1.00	2.96	38.4	6.51
Dihexyl ether	0.79	1.87	-	-
1-Octanol	0.83	7.47	27.1	-

N-alkylpyridinium, tetraalkylammonium, and tetraalkylphosphonium ions. The common anionic parts of the ionic liquids are halides, nitrate, acetate, hexafluorophosphate ([PF_6]), tetrafluoroborate ([BF_4]), trifluoromethylsulfonate ([OTf]), and bis(trifluoromethanesulfonyl)imide ([NTf_2]). Ionic liquids possess exceptional physicochemical properties. Many of them remain in a liquid state at temperatures between 0 and 400 °C. Ionic liquids have low-to-negligible vapor pressures and in many cases show high thermal stability. They may be the most complex of all solvents because they are capable of virtually all possible types of interactions with solutes. Therefore, ionic liquids can solubilize a variety of organic and inorganic compounds. They can be designed to be immiscible or miscible with water and a number of organic solvents [53]. The physicochemical properties of ionic liquids are influenced by both their cationic and their anionic moieties. Han and Armstrong [54], in their review, exemplified several unique changes in the physiochemical properties when ionic liquids are used as solvents. For instance, both the densities and surface tensions of ILs change depending on the type of cations when the same anion is used as counterion and decrease if the length of alkyl chain increases. In contrast, the viscosities of the same group of ionic liquids with the same anion increase with an increase in alkyl chain length. The solubility of ILs depends on the cation and anion as well. For example, 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and [BMIM][BF_4] are soluble in water, while [BMIM][PF^6] and [BMIM][NTf_2] are immiscible with water. Increasing the length of the alkyl chain on the cation lowers the solubility of ILs with [BF4] anions. 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF_4]) is immiscible with water [55]. Combinations of different possible cations and anions result in a large number of ionic liquids with different properties. Therefore, ionic liquids often are referred to as ''tailor-made or tunable materials'' [56]. There are several excellent reviews on this topic covering various aspects of the use of ionic liquids including their applications in separation science [53, 57-59].

Due to these special properties, ionic liquids can be used as a hydrophobic or hydrophilic membrane phase. Consequently, they can be immobilized both on hydrophobic and on hydrophilic supports. For example, for immobilization of the methylimidazolium-based ionic liquid used for the separation of water-soluble ions such as sodium chloride or thymol blue, the hydrophilic polyvinylidene fluoride, polyethersulfone, and nylon were used [60]. Recently, several interesting reports were published concerning applications of SLM separation in which ionic liquids were used as a membrane phase. This type of SLM was used for separation of gases [61, 62], hydrocarbons, including aromatic and aliphatic [63, 64], organic sulfur and nitrogen compounds [65], and other organic compounds like alcohols, amines, or ketones [66, 67]. Despite the fact that ionic liquids are widely used in SLM due to their unusual selectivities, high extraction efficiencies,

durability, and resistance to thermal degradation, more research is necessary on their long-term stability, recyclability, toxicity, and reduction of their water solubility.

5.4. Membrane units (module design)

The main purpose for using the module is to hold the porous polymer soaked with liquid phase in a manner which ensures its mechanical stability, large effective surface area, and free flow of the feed and receiving phases. There are several types of configurations of SLMs which can fulfill this requirement and they are determined by the shape of applied module (see Fig. 3.13). The most popular ones are hollow-fiber SLM (HF-SLM, Fig. 3.13A) and flat-sheet SLM (FL-SLM, Fig. 3.13B). Sometimes other shapes of SLM configurations are also utilized, for example, spiral-wound SLMs (Fig. 3.13C).

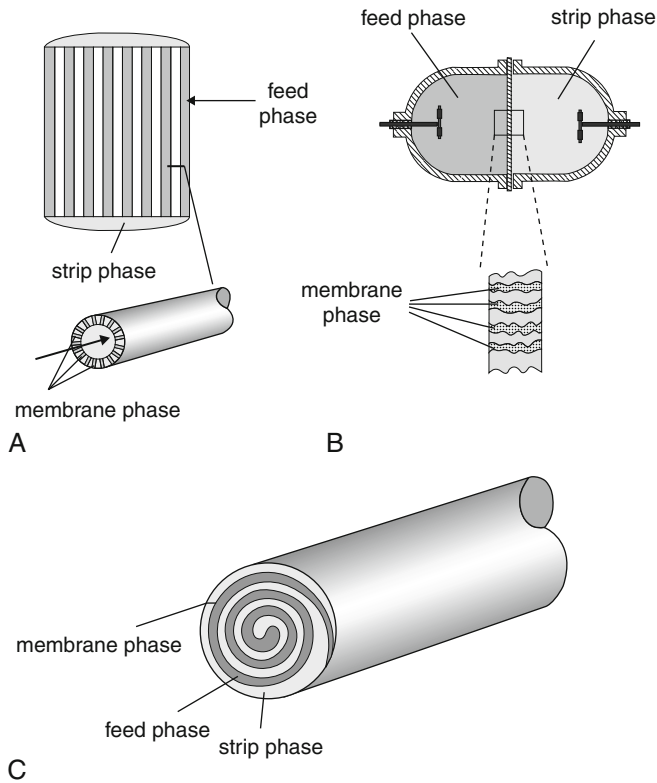

Figure 3.13 SLM configurations (designs): (A) hollow fiber, (B) flat sheet, and (C) spiral wound.

The simplest in design, the flat-sheet SLM, can be utilized on the laboratory scale, but it is difficult to scale it up for industrial applications. Usually, it is a porous polymer membrane whose pores are filled with the organic liquid and carrier, set in between the source phase and the receiving phase, which are being gently stirred (Fig. 3.13B). The design of the hollow-fiber SLM module (Fig. 3.13A) consists of an outer shell, which is a single nonporous material, through which the materials inside cannot be transported. Inside, a certain number of thin fibers are placed along the length of the shell. The source phase is pumped through the system from top to bottom, and the pores in the fibers are filled with the organic phase and the receiving phase is forced out through the sides of the shell. The use of the hollow fibers gives one of the most significant advantages, namely the surface area and membrane thickness resulting in high rate of mass transfer. Another good feature is that the source/receiving phases are easily recoverable. However, there are some drawbacks such as very hydrophobic membrane solvents are required to maintain integrity, and pore fouling often occurs due to surface effects and particles in the system.

The spiral-wound membrane is essentially a flat membrane wrapped around a perforated tube, through which the effluent streams out of the membrane. As can be seen (Fig. 3.13C) that sandwich is actually four layers: a membrane, a feed channel, another membrane, and a permeate channel, which forces all the separated material toward that perforated tube in the center. This type of membrane is an intermediate step between the flat, laboratory membrane and the hollow-fiber membrane, at least in terms of surface area per unit volume and stability.

However, the high surface area is not always the only important factor that has to be considered during SLM module design. Another is the possibility of obtaining a high feed phase/receiving phase volume ratio. Also, it is necessary to fulfill some additional conditions (e.g., sample volume, aqueous phases flow rate) resulting in the specificity of application.

A typical illustration of such an approach is the use of SLM modules in analytical chemistry for sample preparation and enrichment of the analyte. They cannot be too big, since they have to be usable in an analytical laboratory. They also should have the possibility to connect online into an analytical system. Also, they have to be suited to the volume of the sample and flow rate of the aqueous phase(s). If the sample volume is limited and concentration of the analyte is low in the sample, for example, blood or plasma, the module has to be designed to give the possibility of a very low flow rate to increase contact time between the feed and membrane phase (Fig. 3.14).

The typical modules are shown in Fig. 3.14A and B. For sample preparation use, volumes are typically in the 10-1000 μl range. By such design, it is feasible to use SLM as a very efficient sample preparation method for pharmaceutical and environmental analysis [68].

Recently, there has been more attention paid to the miniaturization of the whole analytical system [69]. The simplest way to achieve it in the case

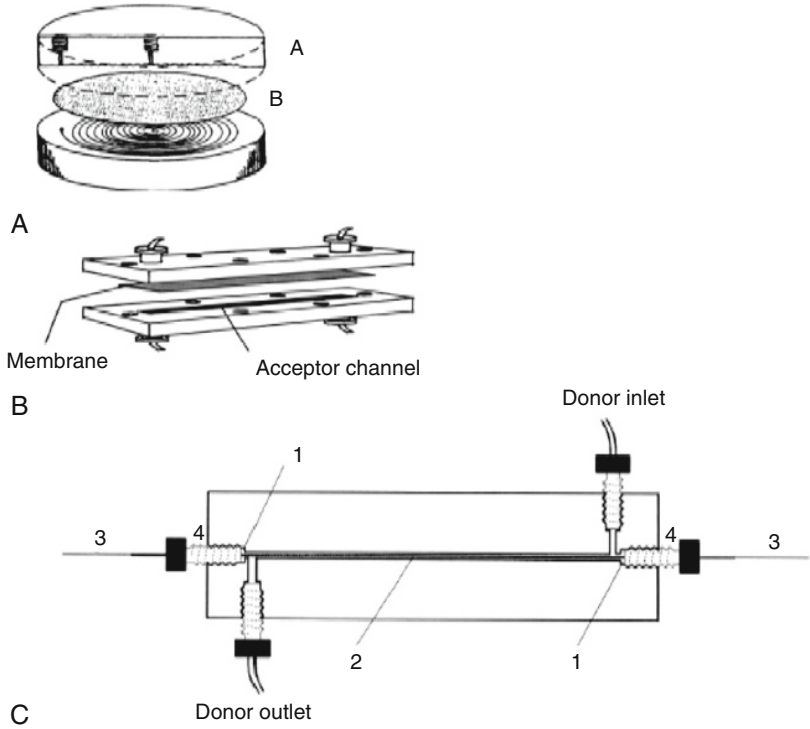

Figure 3.14 (A) Membrane unit with 1 ml channel volume (A, blocks of inert material; B, membrane). (B) Membrane unit with 10 µl channel volume. (C) Hollow-fiber membrane unit with 1.3 µl acceptor channel (lumen) volume (1, O-rings; 2, polypropylene hollow fiber; 3, fused-silica capillaries; 4, male nuts). From Ref. [150] with permission. © 2008 Elsevier.

of SLM is to use a single hollow fiber. There is a possibility to use a membrane previously soaked with liquid and filled-in lumen with a hollow-fiber receiving phase by simple immersion directly in the sample [70–78]. For this type of experiments, there is no need to design a module. However, if there is a requirement to integrate the SLM in an online system, modules have to be designed [79]. This type of unit can have channel volumes around 1 µl (Fig. 3.14C).

6. Membrane Stability

Despite many advantages, SLMs are not often used large scale in industry nowadays. The major reason for this is the membrane stability and lifetime, which are mostly too low to assure good commercial

application. The stability of supported liquid membranes and mechanisms explaining SLM instability, suggestions for stability improvement are discussed in the literature [6, 80]. Since the membrane solvent in SLM is held in the pore structure solely by capillary forces, it is inevitable that during the separation process the solvent is to some extent washed or forced out of the membrane. A complete removal of the membrane phase from one of the pores enables the contact between the feed and strip phases. Once there is a continuous water path in the membrane, it will lead to solute leakage into the strip phase. In the case of carrier-mediated transport, the instability of SLMs occurs due to the loss of membrane solvent and/or carrier from the membrane phase. These effects have an influence on the flux and selectivity of the membrane [81-84]. Depending on the amounts of carrier and solvent lost from the pores of the membrane support, the solute flux might either increase, decrease, or stay almost equal (see Fig. 3.15).

Removal of solvent from the membrane to the water phases increases the carrier concentration in the membrane and therefore increases the flux (Fig. 3.15A). Carrier removal decreases their concentration in the membrane phase, so the flux decreases until the moment when the whole carrier is removed from the membrane and the solute is not transported any more (Fig. 3.15B). In the third possibility when both solvent and carriers are removed from the membrane, the carrier concentration is stable and thus the flux stays equal (Fig. 3.15C). When all of the membrane phase is lost, the membrane breaks down and a direct diffusion between the feed and strip phases takes place.

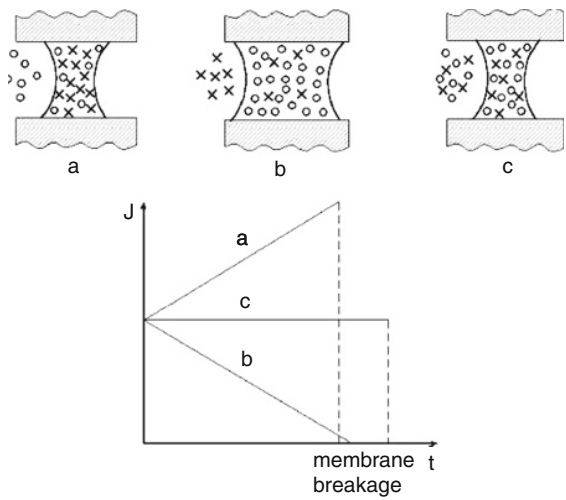

Figure 3.15 SLM degradation and its influence on the flux (*J*) during leakage of (A) organic solvent, (B) carrier, and (C) organic solvent and carrier.

The same problems occur for SLMs using ionic liquids as a membrane phase. Therefore, research studies are focused on the development of new ionic liquids with reduced water solubility [60].

6.1. Factors influencing membrane stability

Many factors, like type and characteristics of the solid polymer support, membrane solvent, and carriers as well as the operating parameters, influence the stability of an SLM. SLM lifetime seems to depend in a clear-cut way on the type of polymeric support and the nature of the liquid membrane, suggesting that solute-solvent and polymer-solvent interactions play a dominant role in membrane stability [85]. Since the membrane solvent is held within the pores by capillary forces, it is clear that the pore structure, morphology, and size influence stability. Asymmetric PTFE membranes with elliptical pores oriented with their major axis parallel to the membrane surface allow a longer lifetime than a polypropylene, polyethylene, or polycarbonate support with essentially straight-through holes [82]. The stability of SLMs strongly depends also on the pore size of the support. Stability of SLMs decreases with an increasing pore size; the smaller the pore size, the longer the observed lifetime of the membrane [86].

The physicochemical properties of organic solvents used as a membrane phase are of great importance in membrane stability. Organic liquid phases exhibit a high viscosity and high organic-water interfacial tension enhances the stability [39, 83]. Hydrophobic aromatic or aliphatic hydrocarbons and ethers are more strongly adsorbed and supported within the pores of a hydrophobic polymeric support than hydrophilic ones. SLMs with *n*-heptane or di-*n*-hexyl ether as a membrane liquid are more stable than those in which ethyl chloroacetate, nitrobenzene, or 1-octanol are used [23, 82]. It is evident that the solubility of membrane phase components in the aqueous phases causes the instability effect. The effect of membrane solvent solubility in water and volatility on membrane stability was investigated [87]. Dozol *et al.* [88] determined aqueous solubility and SLM lifetimes for a numbers of membrane solvents and concluded that a lifetime of over 200 h could be obtained when the solubility of the solvent used is lower than 12 g/l. In carrier-mediated extraction, the stability of SLMs also depends on the kind of carrier and counterion used. For ionic type of carriers, mostly used in SLM, the solubility in the aqueous feed and strip phase is very important. The stability of the membrane increases with decreasing the carrier solubility in aqueous phases. The lifetime of SLMs containing acidic carriers like DEHPA decreases when at least one of the aqueous solutions has a high pH, which is in agreement with the increased solubility of this type of compounds with increasing pH [81]. The stability of membranes in which different aliphatic amines were used as a carrier decreases in the order tertiary > secondary > primary amine, opposite to the carrier solubility [89]. The stability of

Table 3.4 Stability of the supported liquid membranes as a function of the kind of counterion and of the type of organic solvent

	Stability (days)	
Organic solvent	TrpX[a]	Trp DBSA
Di-*n*-hexyl ether	>60	>12
Butylbenzene	>50	>10
o-NPOE	>30	>6
TEHP	>30	>6

From Ref. [23] with permission. © 2008 Elsevier.
[a]X: HCl, PTSA, $HClO_4$ (PTSA, *p*-toluenesulfonic acid; DBSA, dodecylbenzylsulfonic acid).

membranes used for carrier-mediated amino acid transport strongly depends on the type of counterion (Table 3.4) [23]. Furthermore, the stability depends on the flow velocity of the aqueous phases along the membrane. The stability decreases with an increase of the flow velocity by an increasing hydrostatic pressure gradient over the membrane [83].

6.2. Degradation mechanisms

The reason for the instability of SLMs is the loss of the solvent and/or the carrier from the pores of the support, which has an influence on both flux and selectivity. The major degradation mechanisms are dissolution of carrier and membrane solvent in aqueous phases, wetting of the pores in the membrane support by aqueous phases, presence of pressure difference and osmotic pressure gradient over the membrane, emulsion formation in the liquid membrane phase, and blockage of membrane pores by precipitation of a carrier complex [6, 80].

The pressure difference over the membrane exists due to pumping of the aqueous phases through the feed and/or strip channels and has a special importance in hollow-fiber SLM configurations. When the pressure difference exceeds a certain critical value, the membrane phase is pushed out of the pores of the support.

The minimum transmembrane pressure (P_c) required to push the impregnating organic phase out of the largest pores can be calculated using the Laplace equation [84]:

$$P_c = 2\gamma \cos\theta / r, \tag{18}$$

where P_c is the pressure (N/m^2), γ is the interfacial tension between strip or feed solution and liquid membrane phase (N/m), θ is the contact angle between the membrane pores and the membrane liquid, and r is the pore radius (m).

The critical transmembrane pressure calculated using this equation is valid for cylindrical pores. Usually, the commercial hollow-fiber polymeric

supports used for SLM have pores highly irregular in geometry. Therefore, especially for hydrocarbon solvents used as a membrane phase, the P_c is much larger than transmembrane pressure, which indicates that pressure difference is not the main cause of SLM degradation, but the loss of solvent and an emulsification of the membrane phase due to lateral shear forces [80].

The hypothesis for the degradation mechanism of SLMs due to emulsion formation was proposed by Neplenbroek and further developed and extended by Zha *et al.* [83, 90, 91]. The degradation of SLM has been considered to be due to the disruption of emulsion droplets caused by hydrodynamic instability at the surface. In the presence of a surface tension gradient, the interfacial hydrodynamic instabilities could be promoted or damped out, and consequently affect the liquid membrane loss. Neplenbroek observed that the more stable emulsion can be formed by organic solvent used as membrane phase with carrier acting as the emulsifier, the more unstable is the SLM impregnated with this liquid membrane. Therefore, the formation of oil-in-water (O/W) emulsion is a function of molecular structure of the carrier, the type of organic solvent, the counterion type and concentration, and salt contents in the aqueous phases. Many carriers used in SLM, such as ammonium cations (tetraoctylammonium bromide, TOMA) or phosphoric (DEHPA) and long-chain carboxylic acids, are surface-active compounds and can stabilize emulsions. The important parameter for stable O/W emulsion formation is the HLB (hydrophilic-lipophilic balance) scale of the organic phase. The HLB of an emulsifier (carrier) determines the type of emulsion that tends to be formed. The O/W emulsion is formed when the HLB value is in the 8-15 range [84]. An increase in surface area in SLM systems can be due to, for instance, local deformations of the membrane meniscus. When the liquid membrane meniscus is deformed, emulsion droplets can be formed (see Fig. 3.16).

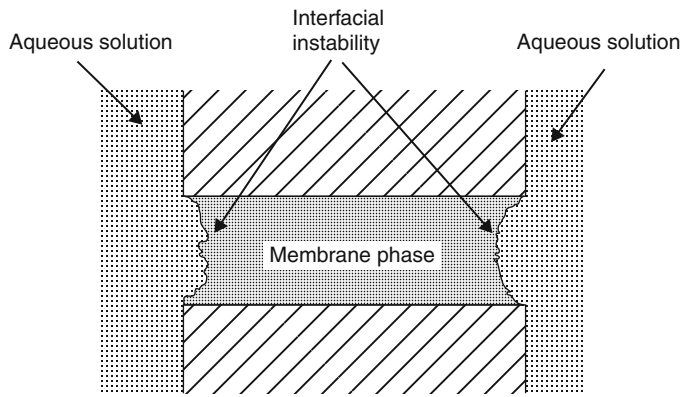

Figure 3.16 Unstable interfaces in an SLM containing microliquid necks. From Ref. [84] with permission. © 2008 Elsevier.

Additionally, the salt content and the type of counterions in the aqueous phases influence the emulsion stability and consequently SLM degradation. It was found that the amount of liquid membrane removed from SLM increases with a decrease in the salt concentration of the aqueous phases and with an increase in their flow velocities [83].

For long-term permeation, there is no one single factor determining the SLM instability. A number of phenomena appear to contribute to instability, including surface shear forces, changes in the membrane morphology, density differences, and membrane preparation protocol [92].

6.3. Improving SLM stability

Supported liquid membrane stability and lifetime limit the industrial application of this separation technique. Therefore, the stability of these membranes needs to be enhanced drastically. A proper choice of the operating and membrane composition factors might improve the lifetime of SLM systems.

The important operating conditions that influence membrane stability are membrane thickness, stirring or flow rate of aqueous phases, carrier concentration, aqueous solute concentration, and operating temperature. In general, larger membrane thickness and lower flow rate increase the stability. Membranes of higher thickness contain more liquid membrane phase and therefore it will take longer before the SLM breaks down. However, increasing membrane thickness results in the flux decreasing due to increasing the diffusion pathway. The SLM stability strongly decreased with increasing the pumping velocity of aqueous phases. This may result in a larger loss of membrane phase due to the larger transmembrane pressure differences and larger shear forces. The SLM lifetime mostly decreases with decreasing the solute and salts concentrations in aqueous phases since there is higher leaching of carrier and larger emulsification [83]. The SLM stability depends also on the operating temperature. The increasing operating temperature increases the solubility of both membrane solvent and carrier in the aqueous phases and membrane lifetime decreases; however, the flux increases due to lower viscosity of the membrane phase [93].

Considering membrane materials, we can distinguish the type of solvent for the carrier and membrane phase, the carrier itself, and the support. Increasing viscosity also increases the lifetime but the fluxes are strongly decreased [94].

Molecular structure and physicochemical properties of the carrier used are important for SLM stability, especially the lipophilicity, surface activity, and its solubility in the membrane solvent. The membrane is less stable when a more surface-active compound is used as a carrier [89]. When the carrier loss is the main reason for the SLM instability, the membrane stability can be increased by attaching the carriers to a polymer or covalently linked onto long aliphatic chains or polysiloxanes [95].

The type of polymeric microfiltration membranes used as a support influence SLM stability in several ways. In general, SLMs using a support with a lower pore size are more stable than those with larger pore size, although the surface porosity should be high enough to obtain a reasonable flux. The pore structure and morphology are also important. Membranes with asymmetric and elliptical pores oriented with their major axis parallel to the membrane surface used as a support give longer SLM lifetime than a support with essentially straight-through holes [96].

There are several other methods, which can be found in the literature, to enhance the stability of SLM, like reimpregnating of the support, stabilization by plasma polymerization, formation of barrier layers on membrane surface, or using sandwich SLM.

The SLM could be regenerated by reloading the membrane supports with fresh liquid membrane solution after they have decayed, which provides the same extraction efficiency as a newly prepared SLM [25]. The regeneration of degraded hollow-fiber liquid membranes could be done in the same way by simply reimpregnating, then pumping the fresh membrane phase at the lumen side of the support for a few minutes instead of the aqueous solution. Continuous impregnation of the membrane is also possible and is mainly applied for hollow-fiber modules. The vertical hollow-fiber module containing one single fiber with a certain amount of liquid membrane phase at the bottom was designed. The membrane liquid from this fiber was soaked into the pores of the support and moved upward through the porous network by capillary forces [97]. The continuous reimpregnation of the support was also done by adding membrane phase as an emulsion to the one of the aqueous phases. It works well, but one of the aqueous phases is still polluted with the membrane liquid [18].

One of the most important degradation mechanisms of SLM is an emulsification of the membrane phase due to lateral shear forces. Therefore, formation of barrier layers on the membrane surface by physical deposition [98] or by interfacial polymerization could prevent instability [99, 100]. A polysulfone support with *N*-methylpyrrolidone as a solvent was coated by a poly(ether ketone) layer as the outside layer and gave a specific composite membrane support. Such composite hollow-fiber membranes showed significant improvement in stability in copper ions permeation.

A plasma polymerization surface coating is another possibility to prevent the supported membrane degradation [101]. This prevention also reduces the surface membrane pores and increases mass-transfer resistance, resulting in a decreased permeability of the membrane system. The stabilization of SLM prepared by impregnating polypropylene glycol (PPG) into the pores of microporous flat-sheet polyvinylidene fluoride (PVDF) or polypropylene (PP) membranes, through crosslinking the liquid membrane phase by using γ-radiation, was reported [102, 103]. These membranes retained both their selectivity and stability over a period of

more than 1 month, and the phenol mass transfer was higher than through silicon rubber tubing membrane.

6.4. Gel SLM

The stability of SLMs can be improved by gelation of the liquid membrane phase using, for example, PVC as gel-forming reagent [83]. The stabilization of SLMs by gelation could be carried out in two different ways: by a homogeneous gelation in the pores of the support and by applying a thin dense gel layer on the feed side of the membrane (see Fig. 3.17). Both gelations of liquid membranes increased the resistance against liquid displacement out of the support by effectively preventing the liquid membrane meniscus from deformation and therefore emulsion formation. However, the stability increases with PVC concentration. Only gelled liquid

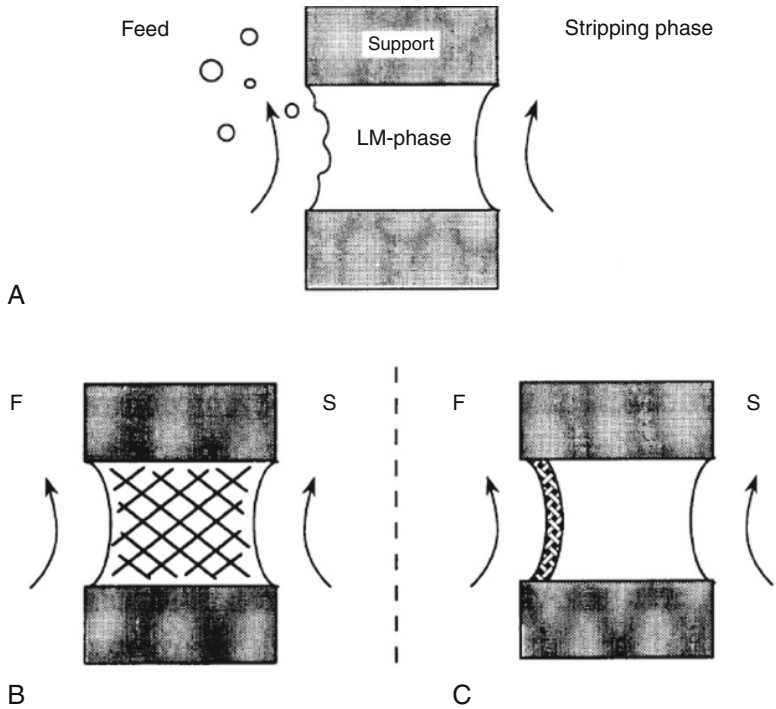

Figure 3.17 Influence of a gel network on SLM stability: (A) without gel network: SLM degradation by emulsion formation (due to local deformation of LM phase in the pores of the support); (B) homogeneous gel network in LM phase; and (C) one thin dense gel layer at the interface with the feed. From Ref. [83] with permission. © 2008 Elsevier.

membranes with low polymer concentration are interesting for practical applications because the diffusion rate of carrier molecules in a gel network decreases drastically with increasing polymer content [83]. In contrast to the result of Neplenbroek, gelation of the LM was not effective in improving the stability when trimethylammonium chloride (TOMA-Cl) and *o*-nitrophenyl were used [80].

6.5. Polymer inclusion membranes

Self-supporting membranes (SLMs) have been used for more than 30 years as polymer membrane ion-selective electrodes. This type of membranes, commonly called polymer inclusion membranes are formed by casting a solution containing an extractant, a plasticizer, and a base polymer such as CTA or PVC to form a thin stable film [104]. A number of other names are also used such as polymer liquid, gelled liquid, polymeric plasticized, fixed-site carrier, or solvent polymeric membranes. The polymeric inclusion membranes are highly resistant to carrier and plasticizer leakage and are considerably more stable than SLM. In PIMs, the carrier, plasticizer, and base membrane are well integrated into a relatively homogeneous thin film. The comparison of SLM and PIM stability has been reported in many papers. Kim *et al.* have investigated the stability of both types of membrane under similar experimental conditions. They reported no flux decline or evidence of material losses within 15 days of continuous transport experiments with PIMs containing CTA, 2-nitrophenyloctylether (2-NPOE) and macrocyclic carrier, while for SLM leakage of the organic material was observed after 48 h [105]. The better stability of PIMs compared to SLMs was also reported for a membrane using Aliquat 336 as a carrier. Under similar experimental condition, PIMs were stable for 30 days, while SLMs only for 7 days [106]. The results of several studies of PIM lifetimes are summarized in Table 3.5.

The good stability of PIMs over the various types of liquid membranes, including SLMs, and the adequate, but lower, permeability and selectivity show the potential practical applications. The main problem is the low mechanical strength of PIMs.

An excellent review providing a comprehensive summary of all aspects of those membranes was published recently [104].

6.6. Integration of SLM with other membrane processes

To overcome the problems with SLM stability, the idea of their integration with other membrane processes was also investigated. Two approaches can be distinguished. Both could lead to significant increase of the liquid membrane lifetime. One approach is to separate the liquid membrane from the feed and receiving phases. It can be achieved by placing liquid

Table 3.5 PIM lifetimes under continuous operation

Membranes (base polymer/carrier/plasticizer)	Reported lifetime and membrane performance
CTA/calix[6]arene/2-NPOE	Small flux decline after 30 days
CTA/lasalocid A/2-NPOE	No sign of flux decline or carrier and plasticizer losses after 10 days. Stable after 10 months storage in air
CTA/acyclic polyether bearing amide/2-NPOE-TBEP	Small flux decline after 15 days but no evidence of carrier and plasticizer loss
CTA/calix[4]arene/2-NPOE	Small flux decline after 20 days but no evidence of carrier and plasticizer loss
CTA/calix[4]arene/2-NPOE	Stable flux after 1 month
CTA/DC18C6/2-NPOE-TBEP	Flux decline began slowly after 100 days but no evidence of carrier and plasticizer loss
CTA/Aliquat 336/2-NPOE, DOS, DOTP, or DOP	Flux decline and carrier/plasticizer loss began after 30 days
CTA/Aliquat 336/T2EHP	Flux decline began after 18 days
CTA/*t*-BuDC18C6/2-NPOE-DNNS	Stable for several weeks

From Ref. [104] with permission. © 2008 Elsevier.
TBEP, tri(butoxyethyl)phosphate; DC18C6, dicyclohexano-18-crown-6; DOS, dioctylsebacate; DOTP, bis (2-ethylhexyl)terephthalate; DOP, dioctylphthalate; *t*-BuDC18C6, *t*-butyldicyclohexano-18-crown-6; DNNS, dinonylnaphthalenesulfonic acid.

membrane between two pieces of porous membranes. If solid membranes are not involved in the transport of the solute, but are only passively separating such a system, we have stagnant sandwich liquid membranes (SSwLMs) [107-109]. For example, such a system was used for transport of Cu(II) ions using DEHPA as a carrier and *n*-decane as the organic solvent. The sandwich membrane shows higher copper flux and longer lifetime (100 vs. 5 h) in comparison with SLM [107] (for details, see Chapter 5).

However, it is also possible that the two stagnant membranes not only are used as barriers for liquid membrane protection but also actively take part in the transport of solute. This gives an opportunity to increase membrane stability and also the selectivity of the separation. In this case, very often the term hybrid liquid membrane (HLM) is used. In most cases, such a system comprises the bulk liquid membrane placed between two solid ion-exchange membranes. Here both ion-exchange membranes are barriers, which physically separate the organic and aqueous liquid phases. Moreover, the ability of those membranes to charge species sorption from aqueous solution causes a high accumulation of reacting species at the interfaces. Many applications have been described [4, 110-123]. The typical

example of a hybrid (integrated) membrane system in which liquid membrane is used was presented by Wódzki *et al.* [122]. In their study, poly (oxypropylene) bisphosphates were synthesized by modification of various polypropylene glycols and used as macroionophores of metal cations [K(I), Na(I), Ca(II), Mg(II), Zn(II), and Cu(II)]. In a comparison of the supported and hybrid liquid membranes [120], competitive transport of an equimolar mixture of cobalt(II) and nickel(II) was investigated. In both types of membranes di-2-ethylhexyl phosphoric acid (D2EHPA) as well as commercial extractants, that is, Cyanex® 272, 301, and 302 were used as ion carriers. The HLMs were composed of the cation-exchange membranes with bulk liquid membrane in the system: cation-exchange membrane-organic phase-cation-exchange membrane. After studying several factors that influence cation transport selectivity and transport effectiveness it was found that the separation of Co(II) from Ni(II) is governed by the ionic carrier used as well as by the acidity of the aqueous source phase. Interestingly, in the HLM processes, lower metal ion fluxes than in supported liquid membranes processes were observed. However, higher separation coefficients for Co(II) from Ni(II) were found for hybrid than for SLMs (for details, see Chapter 5).

The other approach to increase stability of the SLM and simultaneously alter the efficiency of the separation is to prevent the loss of liquid membrane phase by using the so-called SLM with strip dispersion. This concept was developed by Ho [124, 125]. An aqueous strip solution is dispersed in an organic membrane phase solution containing an extractant in a mixer, and the water-in-oil dispersion formed is then pumped to contact one side of a microporous support. As a result, these droplets are retained in the strip dispersion side and cannot pass through the pores to the feed solution side. The constant supply of organic membrane solution into the pores ensures a stable and continuous operation. Moreover, the direct contact between the organic and strip phases (with high-shear mixing, if necessary) provides efficient mass transfer for stripping. This process is a combination of two supported liquid membranes and emulsion liquid membrane simultaneous separation and sometimes is called strip dispersion hybrid liquid membrane (SDHLM) separation [127, 128]. For SLM with strip dispersion, the main aim is to stabilize the liquid membrane into the pores of the polymeric support by preventing emulsification of organic phase. Mostly, an SLM/strip dispersion process is used for metal separations [124–136] as well as for separation of organic substances, for example, organic acids and penicillin G [130, 137] and can be realized both in flat-sheet LM and in hollow-fiber LM. In the second case, the separation process is called [134–136] the pseudoemulsion-based hollow-fiber strip dispersion (PEHFSD) technique, but it is not different in principle from the original concept of Ho, who used a hollow-fiber polypropylene support in his pioneering study on removal and recovery of metals from wastewater and process streams.

In conclusion, there is no universal benchmark for membranes with satisfactory lifetime, permeability, selectivity, and mechanical resistance needed for industrial application. For practical purposes, a compromise between stability and efficiency is needed.

7. Supported Liquid Membranes Application

As described above, there are a variety of possibilities to design SLM processes for various purposes depending on the requirements. On the one hand, we have the simplicity of the realization of the separation/transport process and, on the other hand, its significant flexibility for adaptation. In fact, any system in which it is feasible to incorporate liquid or solution of carrier into the pores of the polymer—independent of its size, shape, or geometry—which separates two other liquid, immiscible phases, can be treated as an SLM. Moreover, it is possible to multiply such systems by proper manipulation of the manifold. Taking into account these features of SLMs, it is not surprising that there is much interest in this separation method in various fields including analytical, inorganic, and organic chemistry, hydrometallurgy, chemical engineering, biotechnology, and biomedical engineering. In fact with SLM separation, it is possible to separate various types of chemical compounds from gases or inorganic ions through many organic compounds (charged or uncharged species, hydrophobic to hydrophilic, stereoisomers, etc.) to large molecules (e.g., peptides or even proteins). Obviously, all applied approaches have their specific separation requirements depending on the nature of the separated compound, matrix composition, and also on the goal of the studies.

What follows are selected examples of applications. The aim is to show how the concept of liquid membranes is utilized in various fields where efficient separation is required. We hope that it will give the reader a better understanding how the theoretical and laboratory studies carried out to explain the transport phenomena through liquid membranes can be applied to solve a variety of separation challenges that can be encountered in real life.

7.1. Analytical applications

An essential step in the development of almost every analytical method is sample preparation. This process, no matter how it is performed, should remove potential interferences, increase the concentration of the analyte, and be reproducible independently of the sample matrix variation [138]. In recent years, several trends have emerged, such as the use of smaller initial sample sizes, small volumes or no use of organic solvents, enhancement of the specificity and selectivity, and increased automation [138]. Many techniques

have been used to achieve one or all of those goals including solid-phase extraction (SPE) or liquid-liquid extraction (LLE) and also membrane techniques [138, 139]. For membrane separation, one possibility is to apply the SLM concept in achieving the goals of sample preparation. SLM extraction as a sample pretreatment technique was developed at Lund University in Sweden by Audunsson for enrichment of amines [140]. Since then SLMs have begun to be widely applied for sample cleanup, enrichment of various types of chemical substances such as metal ions, organic acids, amines, amino acids, phenolic compounds, peptides, herbicides, and drugs (Table 3.6).

Many applications have been reviewed [5, 27, 68, 151–154]. The practical and theoretical aspects of SLM extraction from an analytical chemistry point of view are extensively presented; therefore, they will not be described here. However, we would like to present some examples to show that knowledge gained from basic studies on the liquid membrane transport can be utilized to solve practical problems in sample preparation.

The first example comes from the field of environmental chemical analysis and considers SLM enrichment and determination of triazine herbicides from natural water samples [141]. It shows how simple manipulation of donor and acceptor phase pH, the simplest manner of transforming the analyte into a transportable form, can lead to an SLM system with high extraction efficiency. A porous PTFE membrane impregnated with water immiscible dihexyl ether was used as an organic solvent. The obtained detection limit of triazines ranged from 0.03 to 0.16 μg/l in natural waters with 20 min extraction time using simple UV detection.

A similar concept was used for other environmental applications, for example, phenoxy acids, sulfonureas, phenolic compounds, and other environmentally important persistent pollutants [68, 76, 141, 143, 155-166]. Also, in the same manner, several drugs were enriched and determined in body fluids such as urine [144-146, 167-172] or blood [147, 156, 157, 173, 174]. A very advanced application of SLM for analytical purposes, where transport process was based on simple diffusion with pH adjustment of aqueous phase, is the extraction of the basic drug, bambuterol, for pretreatment of plasma samples before analysis with capillary zone electrophoresis (CZE) [147]. Bambuterol was used as a model substance in a separation system, where either 6-undecanone or a mixture of di-*n*-hexyl ether (DHE) and tri-*n*-octylphosphine oxide (TOPO) was used as membrane phase. It was possible not only to achieve a very low limit of detection (~50 nmol/l) but also to ensure the removal of salts from the sample. It helped to obtain the low ionic strength of the blood plasma samples and permitted subsequent sample stacking in the capillary electrophoresis step.

In SLM extraction of metals or small multifunctional organic compounds a more difficult situation is encountered. In an aqueous environment, they are permanently charged within all pH ranges. Therefore, their affinity toward the organic phase is very low and as a result transport efficiency is

Table 3.6 Selected applications of SLM for sample preparation

Compound(s)	Sample origin	Transport mechanism, conditions	References
Trazines	Environmental	Simple diffusion, adjustment of aqueous phases	[141, 142]
Phenoxy acids	Environmental	Simple diffusion, adjustment of aqueous phases pH	[143]
Aminoglycoside antibiotics (neomycin, gentamicin, streptomycin)	Food, environmental	Simple diffusion, adjustment of aqueous phases pH	[144]
Amphetamines	Pharmaceutical	Simple diffusion, adjustment of aqueous phases pH	[145]
17β-estradiol and its metabolites	Food, environmental	Facilitated diffusion, TOPO used as carrier, adjustment of aqueous phases pH	[146]
Bambuterol	Pharmaceutical	Facilitated diffusion, TOPO used as carrier, adjustment of aqueous phases pH	[79, 147]
Metals (Cu, Cd, Co, Ni, Zn)	Environmental	Simple diffusion of the metal complex formed with 8-hydroxyquinoline in donor phase, adjustment of aqueous phases pH	[20]
Pb	Environmental	Counter-coupled carrier-mediated transport, D2EHP used as carrier, adjustment of aqueous phases pH	[148]
Peptides	Pharmaceutical	Counter-coupled carrier medieted transport, Aliquot 336 used as carrier, adjustment of aqueous phases pH	[149]
N-(phosphonomethyl) glycine (glyphosate)	Food	Counter-coupled carrier-mediated transport, Aliquot 336 used as carrier, adjustment of aqueous phases pH	[150]
Polyamines	Pharmaceutical	Counter-coupled carrier-mediated transport, D2EHP used as carrier, adjustment of aqueous phases pH	[73]

very limited. Several solutions have been proposed to overcome this. A good illustrative example of the transport of ionic species is SLM extraction of metal cations [20]. The possibility of using an SLM for the enrichment of five metals (Cu, Cd, Co, Ni, and Zn) in a flow system with offline atomic absorption spectrometry in the final analysis step has been investigated. Different approaches to transport metals across the membrane were demonstrated. In one system, 8-hydroxyquinoline was used as chelating agent in the sample (donor) solution and metal ions were extracted as a neutral complex by simple diffusion. In a second system, potassium thiocyanate was used in the donor solution and a cationic carrier (Aliquat 336) in the membrane liquid. In a third system, 8-hydroxyquinoline was used in the donor solution and Aliquat 336 in the membrane liquid. The extraction efficiency was generally better for facilitated extraction but it was dependent on the type of metal cation extracted. The approach utilizing carrier-mediated transportation of metal ions was further developed in a series of studies of Djane *et al.* [148, 175–177]. In this case, the SLM extraction of metal cations was realized by the use of anionic extractant D2EHP (di-2-ethylhexyl phosphoric acid), which served as a complexing agent incorporated into an organic liquid membrane. High extraction efficiency was strongly influenced by the acceptor and donor phase pH, which confirmed the counter-mediated carrier transport mechanism. By using D2EHP, it was feasible to determine lead in urine samples [148, 176] and other toxic metals in river water [175]. A similar approach was used for organic multifunctional compounds. As mentioned before, the simplest example is an amino acid with two functional group of opposite acid/base properties. The possibilities of realizing the amino acid transport were presented in several reports [25, 26, 178]. Similarly to metal extraction, achieving high flow rates in simple diffusion by converting the amino acid into its hydrophobic derivative and proper adjustment of the phase pH led to significant increase of extraction efficiency [178]. The use of cationic [25] or anionic [26] hydrophobic carriers and proper choice of aqueous phase pH also makes it possible to extract amino acids with high extraction efficiency. This concept was used for SLM extraction of other multifunctional substances including aminophosphonic acids, peptides, and polyamines from aqueous samples [149, 150, 179–183].

7.2. Applications of the supported liquid membrane technique in biotechnology and environmental science

SLM technology, as already mentioned, has application in many separation processes where selective recovery is one of the main requirements. Several interesting examples of SLM use for separation of various chemical species will be presented to show its flexibility and adaptability for very different purposes (Table 3.7). Additionally, the examples show the potential for the use of SLM technology in industrial processes.

Table 3.7 Examples of SLM application in biotechnology and environmental science

Substance	Application	Liquid membrane	Support	Configuration	References
Fructose	Removal from fermentation broth	Boronic acid derivative dissolved in 2-nitrophenyloctyl	PP	Flat sheet, hollow fiber	[184]
Phenol, cresols	Removal from wastewaters	Natural oil (e.g., palm) liquid membrane	PP, PTFE	Flat sheet	[185]
Chromium(VI) ions	Removal from wastewaters	A commercial amine liquid membrane	PP	Flat sheet, hollow fiber	[186]
Copper	Recovery from spent ammoniacal etching solutions	LIX54 extractant in kerosene	PP	Hollow fiber	[187]
Uranium (U), plutonium (Pu)	Removal from postnuclear plant wastewater	Tri-*n*-butyl phosphate in *n*-dodecane	PP	Hollow fiber	[188]
CO_2	Capture from industrial gases (e.g., CH_4/CO_2 mixture)	Aliphatic amine membranes	PVDF	Flat sheet	[189]

In biotechnological processes, one of the crucial problems is the recovery of the bioprocess products. For instance, during the production of ethanol from sugar cane syrup during the selective fermentation of a mixture of glucose and fructose carried out by a mutant *Saccharomyces cerevisiae* strain, a fructose may be obtained as a byproduct. In a fed-batch process, together with main product of fermentation ethanol, fructose is accumulated in the bioreactor, decreasing process performance due to the inhibition of microorganism.

Continuous removal of fructose and ethanol may prevent that inhibition. However, sugar separation is a relatively difficult and expensive task, as the most commonly used commercial method for sugar separation involves chromatographic processes. Di Luccio and coworkers [184] have investigated the feasibility of removing fructose continuously from a fermentation broth using flat-sheet and hollow-fiber SLMs. They used a liquid membrane system based on facilitated transport of fructose using boronic acid derivative dissolved in 2-nitrophenyloctylether as solvent impregnated in a porous polypropylene support. The results show that fructose removal from the fermentation broth can reduce microorganism inhibition and increase the system performance, although further improvement in membrane stability and fluxes are still necessary.

The other interesting SLM application is removal of organic compounds from wastewater, which comprises liquid waste discharged by domestic residences, businesses, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Therefore, there is a constant need to find methods that provide efficient treatment of wastewater in order to clean it up via separation and removal of the toxic substances. SLM technology is an interesting choice for selective elimination of water contaminants. For example, Venkateswaran and Palanivelu [185] investigated the transport of phenol through a flat-sheet SLM containing, interestingly, vegetable oil as liquid membrane. The results obtained show effective removal of phenol using PTFE membrane and PP as a solid support. Among the various oils tested, palm oil was chosen as the best liquid membrane with permeability of 8.5×10^{-6} m/s in acidic feed of pH 2 with 0.2 M sodium hydroxide as an effective stripping agent. They were able to transport all the phenol from the feed side to strip solution, with an initial concentration of 100 mg/l, after 6 h. A concentration factor of 5 has been achieved in the present investigation with 0.2 M sodium hydroxide as trapping reagent. They also used similar methodology to remove cresols to explore the possibility of applying this to industrial wastewater under the optimized conditions for phenol. After 14 h of the transport studies in the phenol-formaldehyde industry wastewater, phenolic concentration in the feed solution was

below a detectable level (1×10^{-2} mg/l). It is an interesting application that demonstrates the use of renewable, cheap, nontoxic, naturally occurring vegetable oils as a novel, green liquid membrane for the recovery of phenol from aqueous solution in SLM.

Other important toxicological contaminants that can be found in wastewaters are metals. Toxic heavy metal ions are introduced to aquatic streams by means of various industrial activities viz. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides, etc., and possess a serious threat to the environment. The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn, etc. These heavy metals are of specific concern due to their toxicity, bioaccumulation tendency, and persistency in nature [190]. The SLM technique has been widely applied for the transport and recovery of almost all important metals from various matrices; an excellent review of all aspect of metal permeation through SLM (covering both theoretical and practical considerations) is available [191]. Here, only some selected recent examples of the use of SLM for metal separation will be presented.

Chromium compounds have received considerable attention because these are used extensively in such industrial applications as electroplating, steelmaking, tanning of leather goods, and corrosion inhibition. Therefore, it is not surprising that this metal can be found in many industrial wastewaters. For example, to selectively separate and preconcentrate Cr(VI) ions, a commercial amine as the membrane liquid on the porous polypropylene support in flat-sheet configuration has been used [186]. In the first step, laboratory-scale experiments were conducted with a batch reactor made of perspex, with a membrane fixed amid the two chambers. The flux of Cr(VI) ions was maximum in very low pH (at 1) and above and below this pH it decreases. Additionally, the Cr(VI) transport through the membrane increases with rise in temperature. Tests of the efficiency of the flat-sheet SLM were conducted with higher Cr(VI) concentration (5000 ppm) for 24 h, at optimized parameters. It was observed that about one fifth of the feed Cr(VI) is left over, while the rest is transported. After the laboratory-scale experiments, the system was scaled up for a preconcentration of Cr (VI), applying the proposed SLM parameters, and using the hollow-fiber (HF) system. The highest enrichment factor (13.8) value was obtained for 50 mg/l whereby all of the metal was transported to the stripping phase and the resulting Cr concentration was 688 mg/l. This system is also a good example of how laboratory-scale experiments are useful for introducing an SLM separation method into large-scale purification.

A similar approach, but for removal of copper, was presented by Yang and Kocherginsky [192]. One of the key steps in printed circuit board production is etching of a thin copper layer. Ammoniacal etching solutions are widely used for this purpose. Earlier an SLM-based method was developed to treat wastewater containing ammonia and copper [187]. In this

instance, an effective hollow-fiber supported liquid membrane (HFSLM) separation for copper recovery from spent ammoniacal etching solutions, where copper is present in much higher concentrations is described. Again, a bench-scale HFSLM system with 1.4 m^2 effective membrane surface area was first used to screen for the optimal hydrodynamic and other operational conditions. Finally, successful pilot-scale experiments were conducted on a hollow-fiber membrane contactor with a surface area of 130 m^2. The process results in copper removal by a factor of 3000 and formation of nearly saturated copper sulfate solution in the sulfuric acid, used as a stripping phase. The stability of the pilot-scale system is promising for further industrial scale-up.

The last example shows that it is also feasible to use SLMs to remove and recover efficiently radioactive metals from nuclear process effluent. By using a microporous hydrophobic polypropylene hollow-fiber supported liquid membrane (HFSLM) consisting of extractant, tri-*n*-butyl phosphate (TBP) as carrier diluted with *n*-dodecane, actinides such as uranium (U) and plutonium (Pu) were removed [188]. It was concluded after modeling and evaluation of the process conditions that it is possible to remove more than 99% of U(VI) and Pu(IV) from process effluent in the presence of fission products when stripping reagent 0.1 M hydroxylamine hydrochloride in 0.5 M HNO_3 was used.

Recently, the increase of the amount of carbon dioxide (CO_2) in the atmosphere has become more and more important. Concerns over global warming following the release of CO_2, the most important greenhouse gas, continue to grow. Therefore, carbon dioxide capture is important for both energy production and environmental preservation [193]. Each year about 28 Gt of CO_2 are released into the atmosphere (1 Gt = 1×10^9 metric tonnes) [194]. The exploration of capture and storage methods for CO_2 is ongoing worldwide. Also, in this field SLM technology was used for its selective capture. Al Marzouqi and coworkers [189] designed and evaluated a method to separate CO_2 from a mixture of CH_4/CO_2. They tested four different amines, the most commonly used solvents in industrial applications for carbon dioxide capture, namely diethylenetriamine (DETA), diaminoethane (DAE), diethylamine (DEYA), and bis(2-ethylhexyl)-amine (BEHA) as immobilized liquids in a facilitated transport membrane, where poly(vinylidine difluoride) (PVDF) porous membrane was used as an inert support for the amine solution. After testing various parameters influencing transport such as amine concentration, CO_2 partial pressure, and operating temperature it was observed that CO_2 permeance decreased with increasing CO_2 feed pressure, whereas the permeance of CH_4 remained constant for all tested amines. The permeance of CO_2 and the selectivity were in the order DETA > DAE > BEHA = DEYA. This order is related to the number of nitrogen atoms per amine molecule, which can be correlated to loading capacity and consequently to amine reactivity with CO_2. The main

conclusion of this study was that it is possible to selectively and efficiently capture carbon dioxide from a gas mixture using amine-based SLM. This method might be a good and cheap alternative to other ways of CO_2 capture.

It can be seen that SLM technology can be applied very efficiently in many different separation processes. Despite the problem of the stability, more and more applications, also on the industrial (or at least semi-industrial) scale are being developed and investigated.

7.3. Separation of stereoisomers

Separation of stereoisomers and particularly enantiomers is a very important issue in separation science due to the relevance of the optically pure materials in the pharmaceutical industry. A detailed description of the possibilities of the realization of this process using SLMs was given earlier in this chapter. Most of the examples regarded SLM application in the fields of organic or supramolecular chemistry, for example, as a helpful tool facilitating an evaluation of the stereoselective binding properties of chiral synthetic receptors (chiral selectors, catalysts, etc.). There are many reports showing the utility of SLM for this purpose [37]. In most cases, the obtained enantioselectivities were low or moderate depending on the chiral carrier and transported compound. However, there are manners to obtain significant enantioseparation and even resolution of racemic mixtures in which SLM is the heart of a separation system (Table 3.8).

The most common manner is incorporation of a chiral species into the membrane phase, but additionally the prepared liquid membrane phase should be introduced and combined with the system, which can provide high mass transfer, for example, by maintaining large membrane surface area. However, to increase the enantioselectivity, it is also important repeatedly to introduce feed phase into contact with the membrane phase. As a result, the enantioseparation can be significantly enhanced. The easiest way to achieve such conditions is to apply hollow fibers as support for a chiral liquid membrane [195-199, 206]. Several carriers were applied as additives in hollow-fiber liquid membranes to enhance stereoselective transport of various small organic compounds. Hydrophobic derivatives or complexes of amino acids *N*-3,5-dinitrobenzoyl-L-alanine octylester [195, 196], copper(II) *N*-dodecyl-L-hydroxyproline [197] were used for the chiral separation of amino acids or organic acids. Another example is peracetylated β-CD [198] applied for resolution of drugs, for example, propranolol. Also, quinidine or quinine derivatives as chiral carriers in SLM separation for efficient resolution of *N*-blocked amino acids were reported by Maximini *et al.* [199] recently. In their studies, a continuous SLM process was developed, in which two HF-liquid membrane modules were used (each consisting of 250 individual polysulfone hollow fibers with a total membrane

Table 3.8 Stereoisomer separation utilizing SLM technique

Compound (enantiomer mixture)	Discriminating agent	Separation principle	References
Amino acids, lactic acid	*N*-3,5-dinitrobenzoyl-L-alanine octylester	Carrier-mediated transport in HFSLM	[195, 196]
Amino acids	Copper(II) *N*-dodecyl-L-hydroxyproline	Carrier-mediated transport in HFSLM	[197]
Propranolol	β-CD	Carrier-mediated transport in HFSLM	[198]
N-blocked amino acids	Quinidine or quinine derivatives	Carrier-mediated transport in HFSLM	[199]
Ofloxacin	Dibenzoyltartaric acid	Carrier-mediated transport in HFSLM	[200]
Amino acid esters	Esterases	Combination of enzymatic process with HFSLM	[201]
2-pentanol 1-phenyloethanol	*Candida antarctica* lipase B (Novozym 435)	Combination of enzymatic process with flat-sheet SLM	[202, 203]
Amino acids	Surfactant-α-chymotrypsin complex immersed in LM	Combination of enzymatic process with flat-sheet SLM	[204, 205]

surface of 0.1 m^2). Two organic liquid phases were incorporated in pores of HFs obtained by dissolution of adamantyl-carbamoyl-11-octadecylthioether quinine (module 1) and adamantyl-carbamoyl-11-octadecylthioether quinidine (module 2) with 1-decanole/pentadecane mixture. Racemic DNB leucine was chosen as a model mixture of enantiomers. After five separation steps, a 99% ee D-enantiomer and a 99% ee L-enantiomer were produced at a transmembrane flux of more than 20 mmol/m^2 h. This process led to resolution of both enantiomers with a degree of purity of 99% and in large

quantities (in g). The single separation gave a moderate enantiomeric excess (60% ee). It clearly shows that multiple SLM separation of the same feed phase can give excellent enantioseparation results.

A hollow-fiber liquid membrane was used in a separation of D,L-lactic acid and D,L-alanine resolution [196]. In this case, the enantioselective transport of solutes performed in one module was facilitated by *N*-3,5-dinitrobenzoyl-L-alanine octylester chiral selector, dissolved in toluene. The maximum D,L-lactic acid separation factor achieved was 2.00 and that for the D,L-alanine was 1.75. In both cases, the D-enantiomer flux was preferred. These values correspond to the enantiomeric excess 33.5% ee and 27.2% ee, respectively, and are not as good as in the first example. However, note that in this case, only one separation step took place and feed phase was circulated in the module.

Another example of the use of HF-SLM separation concerns the resolution of racemic ofloxacin [200]. This important drug, a fluoroquinolone antibiotic with one chiral center, was separated in chiral systems by hollow-fiber liquid-supported membrane technology combining with countercurrent fractional extraction. The two chiral solutions contained L-dibenzoyltartaric acid and D-dibenzoyltartaric acid in 1-octanol, and flowed through the lumen side and the shell side of fibers, respectively. The solution which flowed through the lumen side of fibers also contained racemic ofloxacin. The wall of hollow fibers was filled with an aqueous of 0.1 mol/l Na_2HPO_4/H_3PO_4 buffer solution of pH 6.86 containing 2 mmol/l of cetyltrimethylammonium bromide for 48 h. The obtained optical purity for ofloxacin enantiomers was up to 90% when 11 hollow-fiber membrane modules of 22 cm in length in series were used.

We can also obtain an enantiopure compound from its racemic mixture with SLM by using a chemical process that transforms only one of the enantiomers. Together with the SLM separation of either the remaining unreacted enantiomer (or converted into another compound) the enantiomer's resolution was achieved. To ensure a high conversion ratio and transport, both processes should be conducted simultaneously. In most cases, an enzymatic reaction, which gives high enantioselective conversion of the racemic substrate, is used for this purpose. One interesting example was presented by Ricks and coworkers [201]. The resolution of racemic phenylalanine esters with esterases was investigated in relation to the development of a continuous process based on the use of hollow-fiber/liquid membrane (SLM) reactors. They obtained high enantioselectivity when phenylalanine isopropyl ester, whose *R*-enantiomer was converted by subtilisin Carlsberg to *S*-phenylalanine (up to 95% ee), in water at pH 7.5 and temperature 25 °C. The unreacted *R*-enantiomer of ester was removed from the reaction medium via transport of 33% *N*/*N*-diethyldodecanamide/67% dodecane organic liquid membrane through to the feed solution,

where it was trapped by charging due to the low pH. The obtained enantioselectivity for ester was around 80% ee.

Another example of the enzymatic reaction-SLM separation approach is kinetic resolution of *rac*-2-pentanol. *S*-enantiomer of this compound is a chiral intermediate in the synthesis of several potential anti-Alzheimer's drugs that inhibit amyloid peptide release and/or its synthesis [202]. In this case, the immobilized enzyme *Candida antarctica* lipase B (Novozym 435) was used in the process of *rac*-2-pentanol transesterification, leading to the desired product *S*-2-pentanol. It was separated from the reaction mixture by SLM based on ionic liquid, namely 1-butyl-3-methylimidazolium tetrafluoroborate supported in nylon membrane. After testing various parameters influencing the reaction/separation process, it was possible to obtain a high enantioseparation factor, in the 60-80 range, between *S*- and *R*-enantiomer depending on the vinyl ester used as a cosubstrate of the reaction. Similarly, it was also feasible to resolve racemic 1-phenyloethanol [203], which suggests that this method can be used for other types of enzymatic/supported liquid membrane kinetic resolution of various substrates, not only those involving transesterification.

For production of enantiopure compounds, we can also use an encapsulating surfactant-enzyme complex immersed in the liquid membrane. This concept was applied by Miyako and coworkers [204, 205] to resolve a racemic mixture of amino acids and ibuprofen, a widely used drug in pain relief. Two encapsulated enzymes were used, one present in the liquid membrane which coverts one of the enantiomers into transportable form and so promotes its transport as a reaction product to the receiving phase. In this phase, the product is converted back to the original enantiomerically enriched substrate that was subjected to resolution. For example, to resolve phenylalanine [205], the encapsulated surfactant-α-chymotrypsin complex was immersed into an isooctane liquid membrane phase, and in the feed solution the racemic mixture of phenylalanine was dissolved together with methanol. The enzyme-catalyzed enantioselective esterification reaction took place at the feed-liquid membrane phase interface. The L-ester of phenylalanine produced in the course of the reaction was transported through the organic phase, while D-phenylalanine remained in the feed phase. The L-ester reached the receiving phase where it was converted into L-amino acid by the same enzyme-surfactant complex. Note that this α-chymotrypsin-facilitated SLM system achieved remarkable ee $> 99\%$ for L-phenylalanine at the end of the operation (48 h). A similar system was used (in this case utilizing lipases) for the separation of ibuprofen enantiomers using various ionic liquids as solvents in the membrane phase. The obtained resolution was up to 75% ee and depends on both the type of lipase and ionic liquid [207].

Concluding this short summary on the possibilities of the use of SLM technology for the resolution of stereoisomers, by proper choice of the

method and separation conditions, it is feasible to design process that could provide very clean, enantiopure products. Moreover, SLMs can offer a high level of productivity and flexibility compared to analogous industrial-scale chiral technologies such as chiral chromatography or the diastereoisomeric crystallization method.

8. Future Perspectives

In the examples of SLM applications presented above, the possibility to separate high quantities of compounds using small volumes of organic phases shows that this method is still a very attractive choice when an efficient and selective method is necessary. Also, as a result of the development and commercialization of hydrophobic hollow-fiber membrane contactors, SLM might be applied successfully for industrial purposes. This is due to the high membrane surface per unit of volume with satisfactory liquid membrane stability and that HF-SLM technology is easily scalable. Therefore, there is much research to increase the applicability of SLM in the pharmaceutical and chemical industry, metal separation and recovery, wastewater treatment, gas separation, biotechnology, and analytical chemistry. Many of the new, interesting applications of SLM describe the use of the SLM concept. Thus, in the pharmaceutical industry, SLMs can be utilized in the production processes of fine chemicals and even drugs. One such possibility is already described in this chapter, the resolution of drug enantiomers, the production of which is a very challenging task. The other, also involving the new advance of SLM separation in biotechnology, is to use this technique for recovery of various pharmaceutically important compounds from fermentation broths. SLMs were used to separate and recover such compounds as amino acids, for example, L-valine [4, 208] and antibiotics, including β-lactam or cephalosporin antibiotics [209, 210]. Also, other important substances were separated using an SLM system with the aim of using supported liquid membranes in bioindustrial processes, for example, organic acids from fruit juices [211] and fermentation broth [4], sugars [184, 212], or even ethanol after biotechnological processing [213]. These examples show that SLM can also be used in the future for other significant compounds produced using biochemical systems or in the pharmaceutical industry. Obviously, it requires more intensive study but SLM might be a good and cheap alternative to other separation methods.

Metals separation and recovery is always of importance for industry and the environment. The theoretical and fundamental studies on metal transport through SLMs are advanced but still conducted toward implementation of laboratory-scale parameters to industrial applications [191]. This is related to the increased attention to improvement of selectivity and stability

of SLM in metals separation. The increase of selectivity can be achieved by design and synthesis of new carriers [214-218]. Gain in stability of the SLM is tested by implementation of various configurations of supported liquid membranes, for example, hybrid and activated composite membranes [49] or the combined supported liquid membrane/strip dispersion process [127, 130, 133, 219]. Additionally, more attention is being paid to removal of toxic metals from wastewater effluents using mostly hollow-fiber-based SLM, which is important in environment protection [188, 218, 220-226].

An important field in which SLM separation is also employed and is still being developed is gas separation. Research is being carried out to remove greenhouse gases [61, 227, 228] and in the separation of hydrocarbons such as propylene or propane from olefin and paraffin hydrocarbon mixtures [229]. Very recently, the SLM system was even proposed as a method to remove heat and moisture [230]. In this case, SLMs were the transfer media to recover heat and moisture from exhaust air due to the high moisture diffusivity in the liquid layer. The SLM involved comprises three layers: two hydrophobic porous skin layers and a hydrophilic porous support layer where a layer of LiCl liquid solution was immobilized in the macro- and micropores as the permselective substance and acted as a moisture-capturing agent. As can be seen, there is an interesting future for SLM application in this field.

Another area in which SLMs have interesting prospects is sample preparation in analytical chemistry. Unlike in other fields where a high active area is required, the new trends are toward miniaturization, which in the case of SLM is represented by the liquid-phase microextraction (LPME) method based on porous hollow fibers [231]. The other issues being addressed are to improve automation and high throughput of the analytical methods, in which the SLM system is used as an analyte enrichment method [167, 232-234]. Additionally, the improvement of selectivity of SLM extraction is one of the main areas of interest; see the immuno-SLM method example described earlier. Several improvements in this methodology have recently been reported [35, 36, 235-237].

As can be seen from this short survey concerning current trends in SLM methodology, there is still much interest from researchers in various fields in the use of this separation method. The use of a liquid membrane immobilized in porous polymer has been applied in very surprising and unexpected ways. Even if some of the applications might look very complicated, the SLM concept itself is very easy to use in practice. This is due to its simplicity and significant flexibility. By simple variation of separation conditions, configuration of liquid membranes, use of specific carriers, or utilization of the advantages of various separation mechanisms, a very high selectivity and subsequent efficiency of the process can be achieved. This would not have been possible without the immense effort to understand, explain, and improve SLM transport. Obviously, like every separation method, SLM has several limitations (among them, one of the most important is its stability),

but they can be reduced or in some cases even overcome. As a result, the use of SLMs is, and hopefully will be in the future, a promising and interesting method, which can be a good or even better alternative to other separation techniques.

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