Efficient membrane-based affinity separations for chemical applications: a review

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ABSTRACT

This review examines the recent trends and developments in membrane-based extraction technology, with a focus on supported liquid membrane (SLM) extraction. This paper attempts to review the studies on polymeric membrane extraction, relating to mass transfer, stability, fluxes and performance. Prospects for future research, on the use of membrane extraction for *in-situ* product removal of chiral amines, are

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presented as well. The main challenge of the current state-of-the-art membrane extraction technology is limited SLM-stability. Conventionally, polymeric membrane materials are used as an SLM-support. The use of ceramic membranes, either with or without surface modification, should be looked at as a possible means of stability enhancement. The use of ionic liquids as the solvent for membrane impregnation is already studied intensively in literature. However, the performance of a certain IL is strongly dependent on the system at hand. Techniques such as hollow fibre renewal liquid membranes and polymer inclusion membranes, can also increase membrane stability and are discussed further. Lastly, the industrial application potential of membrane extraction is hindered by the lack of scaled-up pilot plants, which is addressed as well.

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LIST OF SYMBOLS

ϵ	Porosity
τ	Tortuosity
A	Membrane surface area
C_{aq} (and C_{org})	Solute concentration of the aqueous (or organic) phase
C_{aq*} (or C_{org*})	Equilibrium concentration of the aqueous (or organic) phase
$C_{i,0}$	Membrane concentration of solute i at the feed-side interface
$C'_{i,0}$	Feed concentration of solute i at the feed-side interface
$C_{i,F}$	Feed concentration of solute i
$C_{i,L}$	Membrane concentration of solute i at the strip-side interface
$C'_{i,L}$	Strip concentration of solute i at the strip-side interface
$C_{i,S}$	Strip concentration of solute i
D_{aq} (and D_{org})	Diffusivity of solute i in the aqueous (or organic) solution
J_i	Flux of solute i
K_{aq}, K_{org} or K_t	Overall mass transfer coefficient (OMTC)
$K_{d,F}$ (and $K_{d,S}$)	Distribution coefficient at the feed (or strip) interface
P	Partition coefficient of solute i
k_i or $k_{aq,F}$	Local mass transfer coefficient for the boundary layer resistance inside of the hollow fibre or of the aqueous feed phase
k_m or k_{org}	Local mass transfer coefficient for the boundary layer resistance within the membrane or of the organic membrane phase
k_o or $k_{aq,S}$	Local mass transfer coefficient for the boundary layer resistance in the shell side or of the aqueous strip phase
L	Hollow fibre length
R_i	Inner radius of the hollow fibre
R_{lm}	Logarithmic mean radius
R_o	Outer radius of the hollow fibre
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

LIST OF ABBREVIATIONS

α-HIBA	α-hydroxyisobutyric acid
3-HP	3-hydroxypropionic acid
Ac	Acetaminophen
BA	Benzaldehyde
BLM	Bulk liquid membrane
BLR	Boundary layer resistance
BOCMC	Bis-(octyloxy)calix[4]arene-mono-crown-6
Bz-T-DGA	Benzene-centered tripodal diglycolamide
CAPEX	Capital expenses
CBC	calix[4]arene-benzo-bis-crown-6
CC	calix[4]arene-bis-crown-6
CCD	Chlorinated cobalt dicarbollide
CFD	Computational fluid dynamics
CMC	bis-(octyloxy)calix[4]arenemono-crown-6
CNC	Calix[4]-bis-2,3-naptho-crown-6
D2EHPA	Di-(2-ethylhexyl)-phosphoric acid
DBAc	N,N-dibutylacetamide
DGA	Diglycolamide
DHDA	N,N-dihexyldecanamide
DHHA	N,N-dihexylhexanamide
DHOA	N,N-dihexyloctanamide
DiOPA	Diisooctylphosphonic acid ($C_{16}H_{35}O_2P$ or Cyanex 272)

LIST OF ABBREVIATIONS (CONTINUED)

DMTS	Dimethyltrisulfide
DNNSA	Dinonylnaphtalene sulfonic acid
DTDGA	N,N,N′,N′-tetra-(2-ethylhexyl)dithiodiglycolamide
EB	Ethyl butyrate
EDTA	Ethylenediaminetetraacetic acid
EME	Electromembrane extraction
ELM	Emulsion liquid membrane
EPT	Emulsion pertraction technology
EVAL	Poly(ethylene-co-vinyl alcohol)
FEM	Finite element method
HDEHP	Bis(2-ethylhexyl)phosphate
(HF)SLM(E)	(Hollow fibre) supported liquid membrane (extraction)
HFRLM	Hollow fibre renewal liquid membrane
HMW	High molecular weight
IL	Ionic liquid
IPA	Isopropylamine
IS(c)PR	*In-situ* (co-)product removal
Kelex 100	7-(4-ethyl-1-methyloxtyl)-8-hydroxyquinoline
KR	Knudsen resistance
LDH	Lactate dehydrogenase
LIX-63	5,8-diethyl-7-hydroxydodecan-6-oxime
LIX-79	N,N-bis(2-ethyl-hexyl)guanidine
LIX-84-I	2-hydroxy-5-nonylbenzophenone

LIST OF ABBREVIATIONS (CONTINUED)

LLE	Liquid-liquid extraction of solute i
LM	Liquid membrane
M2EHPA	Mono-(2-ethylhexyl) phosphoric acid
MB	Methylene blue
MBA	Methylbenzylamine
MBSE	Membrane-based solvent extraction
MPPA	1-methyl-3-phenylpropylamine
MR	Molecular resistance
MTBE	Methyl tert-butyl ether
MWCNT	Multi-walled carbon nanotubes
NADH	β-nicotinamide adenine dinucleotide, reduced disodium salt hydrate
NPOE	2-nitrophenyloxtyl ether
(O)MTC	(Overall) mass transfer coefficient
OPEX	Operational expenses
PC-88A	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
PDMS	Poly(dimethylsiloxane)
PE	2-phenylethanol
PES	Polyethersulfone
PIM	Polymer inclusion membrane
PLP	Pyridoxal phosphate
PP	Polypropylene
PT	*p*-toluic acid
PTA	Purified terephthalic acid
PTFE	Polytetrafluoroethylene

LIST OF ABBREVIATIONS (CONTINUED)

PTMS	Phenyltrifluoromethyl sulfone
PVDF	Polyvinylidene fluoride
RhB	Rhodamine B
SILM	Supported ionic liquid membrane
(S)PEEK	(Sulfonated) poly(ether-ether-ketone)
SPPESK	Sulfonated polyphenylether sulfone ketone
SR	Surface resistance
T2EHDGA	N,N,N′,N′-tetra-2-ethylhexyl diglycolamide
TBP	Tri-*n*-butyl phosphate
TEHDGA	N,N,N′,N′-tetra(2-ethylhexyl) diglycolamide
TDDGA	N,N,N′,N′-tetra-n-decyl diglycolamide
TFA	Tri-fluoro-acetylacetone
THDGA	N,N,N′,N′-tetra-n-hexyl diglycolamide
TOA	Trioctylamine
TODGA	N,N,N′,N′-tetra-*n*-octyl diglycolamide
TOPO	Trioctylphosphine oxide
TPAMTEB	Bz-T-DGA ligand with iso-amyl groups and methylene spacers
TPAETEB	Bz-T-DGA ligand with iso-amyl groups and ethylene spacers
TPDGA	N,N,N′,N′-tetra-*n*-pentyl diglycolamide
(iPr_3)TREN-DGA	Diglycolamide based on tris(2-aminoethyl)amine (with an isopropyl substituent)
TRPN-DGA	Diglycolamide based on tris(3-aminopropyl)amine
VFA	Volatile fatty acids
VR	Viscous resistance

1 INTRODUCTION

In recent years, more and more membrane applications appear for environmental or economic reasons, e.g. to clean gas or liquid waste streams and to reduce energy consumption. Membrane technology has become a competitive technology for many conventional separation processes, such as distillation, evaporation and extraction [1, 2, 3]. Membrane-based hybrid processes, such as membrane distillation and pervaporation, can be used for applications in seawater desalination and water purification [4, 5]. Membrane technology can be proposed as an alternative for conventional liquid-liquid extraction (LLE), which is based on the mixing and consecutive separation of two immiscible phases [6]. Although LLE is a standard separation process, it suffers from a set of important drawbacks, such as the need for dispersion and consecutive coalescence of the feed and extractant phase [7]. Therefore, membrane extraction has been developed as an alternative to overcome the different hurdles of conventional LLE. This review examines the use of membrane-based extraction technology for industrial applications. The characteristics of conventional LLE, as well as its inherent drawbacks, are set against membrane technology for extractive separations. Many membrane-based extraction possibilities exist, but the focus of this review lies on supported liquid membrane (SLM) technology. The new application of membrane-based LLE for *in-situ* product removal of chiral amines in transaminase reaction processes is also analyzed.

2 MEMBRANE EXTRACTION TECHNOLOGY

In the field of separation technology, there is a large demand for improved or new processes, which are able to compete with existing technologies. It is apparent that

these technologies need to meet stringent requirements, relating to product quality, energy efficiency, cost reduction and environmental legislation. A combination of different processes into hybrid processes is needed to meet the industrial needs. Membrane technology is an example and can be used in many industrial branches, such as chemical, pharmaceutical and metallurgical industries [2, 8, 9]. A possibility is to combine membrane technology with conventional liquid-liquid extraction (LLE), to overcome its inherent limitations.

Liquid-liquid extraction (LLE) is a conventional unit operation in the chemical process industries, used for the recovery of target solutes or removal of impurities from a given stream. The solutes are removed by mixing or contacting a feed phase and a (partially) immiscible solvent or extractant, which is more affine for the target solute(s). Generally, the phase contact occurs by dispersing one phase into the other, after which the dispersed phase is separated and coalesced. The solvent is then recovered by distillation, evaporation, crystallization, filtration or a further extraction step [1, 6, 7, 8]. Although this technology is used frequently in industry, it suffers from different drawbacks. First, solvent selection is not straightforward, due to multiple solvent requirements, such as high selectivity for the target solute(s), easy separation from the extracted product and desirable emulsification behaviour. More specifically, phase separation could be inhibited, if stable emulsions are formed between the feed and solvent. Other solvent criteria, such as non-toxicity and biocompatibility, could be needed for extractions with biological cells [10, 11, 12, 13]. Secondly, equipment design and selection are difficult, since a compromise should be made between efficiency, flexibility and costs. Extraction columns are cost-effective, but show lower efficiency and flexibility. Mixer-settlers and centrifugal extractors, on the other hand, show higher extraction efficiencies, but suffer from higher operational and capital costs, respectively. Additional limitations include loading requirements and flooding restrictions in packed extraction towers [1, 7, 14].

To account for the inherent limitations of conventional LLE, hybrid membrane extraction processes have been proposed as an interesting alternative. A distinction can be made between membrane-based solvent extraction (MBSE), liquid membrane (LM) extraction and extraction using polymer inclusion membranes (PIMs). The first technique, namely MBSE, was already patented by Lee et al. [15] in 1976 as an alternative to LLE-processes. Since then, many papers have studied the MBSE-process further. One of the first reports of further investigation of this process is the publication of Kiani et al. [8] dating from 1984. In MBSE, a membrane is employed to separate the feed and extractant phase. One of the phases wets the membrane pores, i.e. the fluid fills the membrane pores. The membrane has no active function in separation and only immobilizes the feed-extractant interface, which is immobilized at the pore mouths. Advantages of this technique include reduced capital and operating costs, whilst having similar efficiencies as in standard extractors. Furthermore, the consecutive phase separation step of the feed and extractant is avoided. A disadvantage of this technique is the need for solvent regeneration, by membrane-based stripping or distillation, which requires an extra unit operation. A schematic flowsheet of simultaneous membrane-based extraction (MBSE) and stripping (MBSS) with a recirculation of the solvent is presented in Figure 1. Another drawback of membrane contactors is the additional resistance, created by the membrane, which hinders the diffusion between the two phases and slows down the separation [14, 16, 17, 18].

To avoid the need for solvent regeneration and a consecutive stripping step, the use of (un)supported liquid membranes (LM) was proposed. These liquid membranes serve as a barrier between two liquid phases [16, 19]. LM systems are promising for a variety of industries, a.o. analytical chemistry, biotechnology and wastewater treatment [20]. Liquid membranes can be used in three distinct configurations, namely bulk liquid membranes (BLM), emulsion liquid membranes (ELM) and supported liquid membranes (SLM) [21]. These types are depicted in Figure 2.

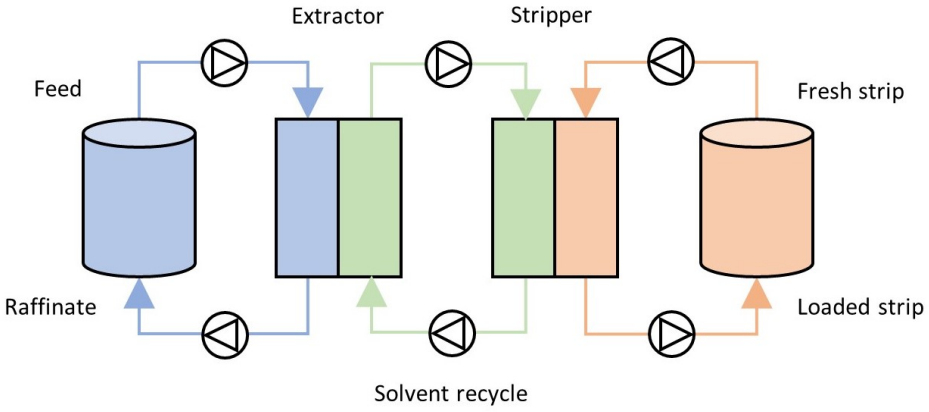


Figure 1: A flowsheet of a membrane-based extractor (MBSE) with a simultaneous regeneration of the solvent by a membrane-based stripper (MBSS), based on Schlosser and Marták [16]. Both contactors generally employ hollow fibres (HF). The solvent flows in the contactor shell in both the extractor and stripper and is recirculated.

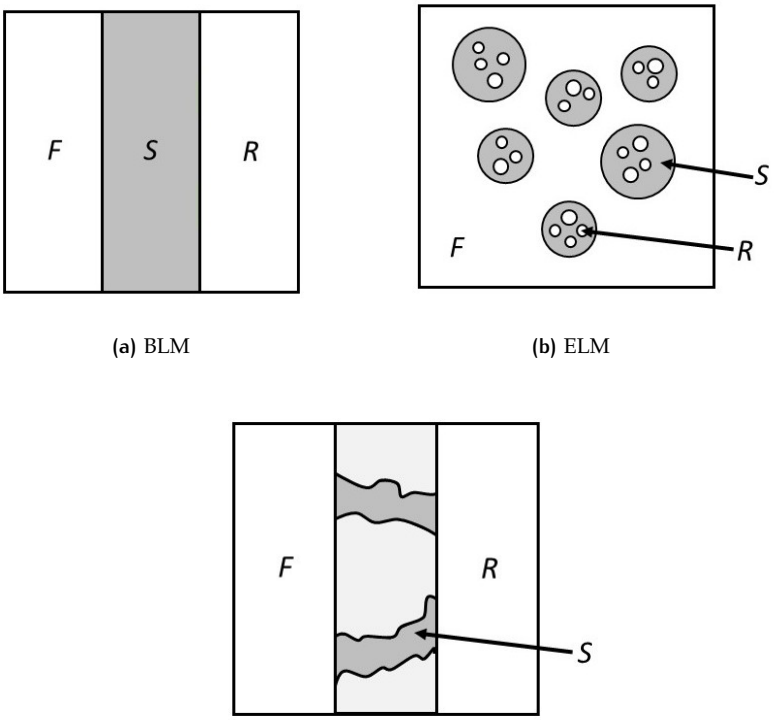
Free or bulk liquid membranes (BLM) are bulk organic phases, which are contacting and separating two aqueous phases. BLMs are deemed to be suitable sample preparation methods for analytical purposes, due to their simplicity in operation, low operating cost and simultaneous separation and preconcentration. However, noticeable disadvantages of BLMs are LM entrainment during extraction, feed contamination by the solvent and frequent emulsification at the LM-surface, limiting its industrial potential [20, 22].

Emulsion liquid membranes (ELM), on the other hand, consist of surfactant stabilized emulsions. More specifically, droplets of an aqueous stripping solution are dispersed within an organic extractant, which is again dispersed in an aqueous feed solution. Solute molecules in the feed are transported to the strip by a facilitated or unfacilitated transportation mode. Unfacilitated transport refers to mass transfer of the solutes solely via diffusion. In facilitated transport, the carrier molecules can bind to the solute and form a solute-carrier complex. This complex diffuses through the membrane phase, which enhances the mass transfer and flexibility of ELM. Furthermore, ELM-systems offer a larger surface area, also improving the membrane transport rate. Although ELMs offer efficient extraction procedures, ad-

ditional problems appear, related to emulsion stabilization and the need for subsequent phase separation of the emulsions. Furthermore, if a high product purity is required, the surfactant removal poses another problem [20, 23, 24].

Supported liquid membranes (SLM) consist of a solid, microporous support in which a liquid extractant phase is immobilized. The liquid remains inside of the pores due to capillary forces. The target solutes are extracted from the feed into the membrane phase and simultaneously stripped by the stripping phase. SLMs have many advantages, such as the relatively small liquid volume which is required in the membrane pores and the tunability of the membrane phase. Furthermore, membrane extraction and stripping are combined in one unit operation [3, 21, 25]. Other advantages of SLM-contactors, such as high interfacial area and no emulsion formation, have already been pointed out in different review papers, by Parhi [21] and Gabelman and Hwang [26] amongst others. A drawback of SLMs is the additional resistance to mass transfer, introduced by the membrane and membrane fouling. However, the most important drawback of using SLMs is the membrane instability regarding long time performance.

The instability is mainly caused by two mechanisms, namely dissolution and emulsion formation of the LM-phase in the adjacent aqueous phases [27, 28]. Additionally, the instability may be attributed to a progressive wetting of the membrane pores by the aqueous phase, a pressure difference across the membrane or the blockage of the membrane pores by precipitation of the carrier complex [29]. Different strategies can be employed to improve SLM-stability, related to the design of LM-separations [30]. A suitable selection of membrane materials and conditions can significantly enhance membrane stability. The use of highly stable polymer materials, such as EVAL [31] and (S)PEEK [32], can ameliorate the stability, as opposed to conventional polymers, such as polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [2]. Other stability enhancements include the formation of barrier layers on the membrane surfaces, surface coating of the mem-



(a) BLM

(b) ELM

(c) SLM

Figure 2: The different types of liquid membranes, namely bulk liquid membranes (BLM), emulsion liquid membranes (ELM) and supported liquid membranes (SLM), with *F*, *S* and *R* the feed, solvent and raffinate solution, respectively. The figures are based on Yurtov and Koroleva [20].

branes and gelation of the LM [28, 29, 33, 34]. Another possibility for stability improvement is the use of ionic liquids as the membrane phase. Ionic liquids are salts showing very low vapor pressures and high thermal stability [35]. If ionic liquids are used to fill the membrane pores, the SLMs are referred to as supported ionic liquid membranes (SILMs). SILMs have high operational and structural stability in liquid-liquid separations, even at high temperature and pressure conditions. The review by Lozano et al. [36] can be consulted for a comprehensive overview of the literature on SILMs before 2011. The use of magnetic ionic liquids in combination with external magnetic fields could even provide a tunable selectivity for the separation of organophilic solutes or gases [37, 38].

As mentioned before, the main limitation of SLMs is their membrane instability. Therefore, polymer inclusion membranes (PIMs), which are a type of liquid membranes, have been introduced. They consist of a liquid phase, with an extractant/carrier, and a base polymer, which provides mechanical strength to the membrane. An additional plasticizer or modifier can be used to improve PIM flexibility or solubility of the target compound. PIMs are significantly more stable and robust than SLMs, although little research is performed, comparing the stability of PIMs and SLMs for a specific application. An important note is that the available literature on PIMs has focused on the use of two base polymers, namely PVC and CTA. However, other materials may be used as well, such as poly(vinylidene fluoride-co-hexafluoropropene), to improve the membrane stability. Cross-linking is another possibility to enhance the stability of PIMs. For a more in-depth overview on the specifics and usage of PIMs in membrane contactors, the review by Almeida et al. [39] can be consulted.

Apart from MBSE and LM-technology, other membrane-based extraction processes exist, such as electro-membrane extraction (EME), which was introduced in 2006 as a novel sample preparation technique. EME is an extraction technique in which an electrical potential is sustained between the sample and the extractant solution, which are separated by a supported liquid membrane. Typically, EME is performed in three-phase mode in which the transition from aqueous to organic and back to aqueous occurs [19, 40]. The EME-setup can be combined with different analysis techniques, such as electrospray ionization mass spectrometry (ESI-MS) [41], high-performance liquid chromatography with UV-detection [42], ion chromatography [43], flame atomic absorption microscopy (FAAS) [44] or with capillary electrophoresis [45]. EME is generally used for sample preparation and micro-extraction procedures with applications in water sample analysis (e.g. herbicides [46], fungicides [47], insecticides [48, 49], phenolic contaminants [50]), biofluids analysis (e.g. determination of drugs in urine [42, 51, 52, 53], blood plasma

[54] or breast milk [55]), determination of plant hormones [56], compound extraction from food samples (e.g. organic acids [43], food colorants [57] and pesticides [58]) and metal ion analysis [59]. Important parameters, influencing the extraction performance are the applied electrical voltage, length of the membrane module, sample volumes and the extraction time. For a more detailed description of the EME-process and its applications and limitations, the reader is referred to the reviews by Drouin et al. [60] and Pedersen-Bjergaard [61].

3 MASS TRANSFER IN MEMBRANE-BASED EXTRACTION

Mass transfer through membranes takes place across interfaces between different phases, namely the feed, membrane and extractant phase. The resistance-in-series-model is mainly used to model membrane contactors in liquid extraction. Furthermore, the use of computational fluid dynamics (CFD) has shown a lot of promise in this field. In this section, attention will be awarded to both modelling tools. For a more in-depth description of other mathematical models, the book by Luis [3] can be consulted.

3.1 Resistance-in-series models

As discussed in the previous section, a distinction can be made between MBSE and SLM-extraction, which also translates into a different modelling approach for both configurations. In MBSE, a solute i may be extracted from an aqueous feed solution by an organic solvent, which wets the pores of a hydrophobic membrane. The mass transfer through the membrane can be caused by the physical solubility of solutes in the solvent or by (bio)chemical reactions. The solute mass transfer in MBSE can

be described by four sequential steps: (1) diffusion through the aqueous boundary layer, (2) equilibrium distribution at the aqueous-organic interface, (3) diffusion through the membrane pores, which are wetted by the organic solvent, and (4) diffusion through the organic boundary layer. Generally, hollow fibre modules are used for MBSE-applications, due to their higher surface area [3, 16, 62]. The mass transfer in a hollow fibre contactor can be described by Fick's law of diffusion and film theory, which assumes that the resistance to mass transfer only occurs in fluid films close to the membrane surface and the membrane itself. For MBSE, the solute flux J_i can be written as [3]:

$$J_i = K_{aq} A (C_{aq} - C_{aq*}) \tag{1}$$

in which K_{aq} is the overall mass transfer coefficient (OMTC), A is the membrane surface area, C_{aq} is the solute concentration in the aqueous solution and C_{aq*} the equilibrium concentration in the aqueous phase [3]. For stripping of a solute or MBSS, the following equation can be used [62]:

$$J_i = K_{org} A (C_{org} - C_{org*}) \tag{2}$$

which employs similar definitions of K_{org}, C_{org} and C_{org*} as in Equation 1 [62]. The analysis of the OMTC is of utmost importance, since this parameter determines the required extraction time and thus equipment size and cost. If the organic phase flows inside of the fibres and no chemical reaction or an instantaneous chemical reaction occurs at the interface, the OMTC can be related to individual mass transfer coefficients (MTCs), as follows [3]:

$$\frac{1}{K_{aq}} = \frac{1}{k_i} + \frac{R_i}{P \cdot k_m \cdot R_{lm}} + \frac{1}{P \cdot k_o} \frac{R_i}{R_o} \tag{3}$$

in which P is the partition coefficient or distribution ratio, and R_i and R_o are the inner and outer fibre radius, respectively. The MTCs inside of the fibre, within the membrane and outside of the fibre are represented by k_i, k_m and k_o, respectively [3]. R_{lm} is defined as the logarithmic mean radius, which is calculated as follows [63]:

$$R_{lm} = \frac{R_o - R_i}{\ln\left(\frac{R_o}{R_i}\right)} \tag{4}$$

If the aqueous phase fills the hollow fibres, the OMTC-formula can be rewritten as follows [62]:

$$\frac{1}{K_{aq}} = \frac{1}{k_i}\frac{R_o}{R_i} + \frac{R_o}{k_m \cdot R_{lm}} + \frac{1}{P \cdot k_o} \tag{5}$$

For stripping, this would translate to [62]:

$$\frac{1}{K_{org}} = \frac{P}{k_i} + \frac{R_i}{k_m \cdot R_{lm}} + \frac{1}{k_o}\frac{R_i}{R_o} \tag{6}$$

As is visible from the equations above, every resistance (namely in the feed, membrane and extractant phase) is represented mathematically by the inverse of the individual mass transfer coefficient. The overall resistance equals the sum of the individual resistances. This model is referred to as the resistance-in-series model, which is analogous to electrical circuits. This model is a simple tool for the analysis of mass transfer through porous membranes [3]. The MTCs can be calculated by simple correlations, such as the Lévêque-correlation for k_i [62]:

$$Sh = \frac{k_i \cdot 2R_i}{D_{aq}} = 1.62\left(Sc \cdot Re \cdot \frac{2R_i}{L}\right)^{1/3} \tag{7}$$

in which D_{aq} is the diffusivity in the aqueous solution, L is the fibre length, and Sh, Sc and Re are the Sherwood, Schmidt and Reynolds numbers, respectively. If

the pores are filled with the organic solvent, k_m can be calculated by the following formula [62]:

$$k_m = \frac{\epsilon \cdot D_{org}}{\tau(R_o - R_i)} \tag{8}$$

in which ϵ is the porosity, D_{org} is the diffusivity in the organic phase and τ is the tortuosity. For the MTC-determination at the outside of the fibre, many empirical correlations have been published, related to flow type and the used hollow fibre module (refer to a.o. Gabelman and Hwang [26], Prasad and Sirkar [64], Figueroa and Weber [65], Lipnizki and Field [66]). As can be seen from the previous equations, the distribution ratio of the solute between the different phases strongly influences the MTC at the partitioning aqueous-organic interface. Therefore, this ratio also determines which resistance is dominating the mass transfer behaviour. The resistance-in-series model thus provides an interesting tool for mass transfer modelling in MBSE- and MBSS-applications [3, 62].

As opposed to MBSE, the mass transfer through supported liquid membranes occurs via two interfaces, namely the feed-membrane and membrane-strip interface. Therefore, the mass transfer in SLMs can be described by the following consecutive steps: (1) convective transport from the feed bulk to the feed-membrane interface, (2) partitioning between the feed and liquid membrane phase, (3) diffusion across the liquid membrane due to the presence of a concentration gradient, (4) partitioning between the liquid membrane phase and the strip bulk, and (5) convective transport from the membrane-strip interface to the strip bulk. The concentration profile of a certain solute i through an SLM is represented in Figure 3.

The solute flux J_i through these membranes can be written as [3, 63]:

$$J_i = K_t(K_{d,F}C_{i,F} - K_{d,S}C_{i,S}) = K_t\left(\frac{C_{i,0}}{C'_{i,0}}C_{i,F} - \frac{C_{i,L}}{C'_{i,L}}C_{i,S}\right) \tag{9}$$

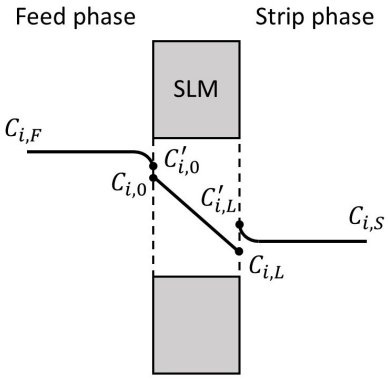


Figure 3: Concentration profile of a compound in a supported liquid membrane, based on Luis [3].

in which $C_{i,F}$ and $C_{i,S}$ are the concentrations in the bulk feed and bulk strip, respectively. The distribution coefficients $K_{d,F}$ and $K_{d,S}$ are defined as the concentration ratios at the feed and strip interfaces. The used concentrations are defined in Figure 3. For SLMs, the mass transfer resistance K_t can be written as [3, 63]:

$$\frac{1}{K_t} = \frac{K_{d,F}}{k_{aq,F}A_F} + \frac{1}{k_{org}A_{lm}} + \frac{K_{d,S}}{k_{aq,S}A_S} \tag{10}$$

$$\frac{1}{K_t} = \frac{1}{2\pi L\epsilon}\left(\frac{K_{d,F}}{k_{aq,F}R_i} + \frac{1}{k_{org}R_{lm}} + \frac{K_{d,S}}{k_{aq,S}R_o}\right) \tag{11}$$

The MTCs inside of the fibre at the aqueous feed side, within the membrane, and outside of the fibre at the aqueous strip, are represented by $k_{aq,F}$, k_{org} and $k_{aq,S}$, respectively. K_t consists of three resistances: the first term occurs due to the resistance at the feed-organic interface at the inside of the fibre, the second term is due to diffusion of the solute-carrier complex across the liquid membrane, and the third term represents the resistance at the organic-strip interface at the outside of the fibre. The MTC in the organic or membrane phase can be calculated as [3, 63]:

$$k_{org} = \frac{D_{org}}{\tau \cdot (R_o - R_i)} \tag{12}$$

in which D_{org} is the diffusivity and τ the tortuosity of the hollow fibre. D_{org} of the solute-carrier complex can be calculated by the Stokes-Einstein equation for porous media. The MTC within the fibre, can be described by the Lévêque-equation, as described earlier [63].

The resistance-in-series model is mainly used for the analysis of solutes mass transfer through membranes, which enables the estimation of extraction efficiencies and overall process performance. The influence of different process parameters (such as feed concentration, process temperature, flow rates, etc.) on the mass transfer can be analyzed by this approach as well [63]. The dominant mass transfer resistance can be determined, which aids in the optimization of the process performance. Tables 1, 2 and 3 give some key examples of mass transfer modelling studies of membrane extraction processes based on the resistance-in-series model. These models are used frequently, as can be seen from the large range of applications for these models, such as uranium recovery [63] and the removal of organics [67, 68, 69], rare earth elements [70, 71] germanium [72] and metal ions [73, 74].

Dixit et al. [63] tested uranium recovery from nuclear waste using a hollow fibre dispersion liquid membrane. By using 30 % TBP as the carrier, more than 98 % of the uranium was extracted from the lean source within 10 minutes, showing its performance. A resistance-in-series model was used to determine the OMTC, similar to Equation 11, but the third term was omitted, due to the presence of an instantaneous stripping reaction. The mass transfer coefficients of the aqueous feed and organic membrane phase were calculated as 1.43 $10^{-}3$ and 5.57 $10^{-}5$ cm/s, respectively. This indicates that the membrane mass transfer through the organic phase was the rate-controlling step. The experimental OMTC of the uranium extraction process was determined as 2.174 $10^{-}2$ cm/s, which showed good agreement with the modelled value of 2.49 $10^{-}2$ cm/s. The model was able to predict the uranium transport rate, even with varying concentrations, flow rates, equipment dimensions and membrane parameters.

The removal of organics was studied by Hao et al. [67], Praveen and Loh [68] and Zhang et al. [69]. Hao et al. [67] studied the recovery of the antibiotic Cephalexin by supported liquid membranes, employing an organic (SLM-OD) or strip dispersion (SLM-SD). Aliquat-336 was used as the extractant in a hollow fibre module. A mathematical model was developed to determine the overall mass transfer coefficients, which were validated with experimentally determined MTCs. The model showed good agreement between the experimental and theoretical MTCs with a relative error of less than 15 %, for varying carrier concentrations. The effects of various operating parameters were studied, such as the carrier concentration and organic-to-feed ratio. The optimal parameters were determined to be 2.5 wt% of Aliquat-336 and an organic-to-feed ratio of 80:500, for which the MTC was 3.56 $10^{-}7$ m/s. This value of the MTC was 30 % higher than obtained with the SLM-OD configuration.

A study by Praveen and Loh [68] checked the extraction and stripping process of phenol using hollow fibre membranes, impregnated with TOPO. More than 97 % of the initial phenol could be removed by the extraction process and the membrane remained stable for 10 cycles of operation. The authors found that the mass transfer kinetics of phenol were best described by a pseudo-first-order diffusion model, whilst the Langmuir isotherm was used to model the distribution equilibrium. A mathematical model, employing the resistance-in-series approach was developed to describe the mass transfer. Excellent agreement was obtained between experimental and simulated data up to phenol concentrations of 2000 mg/L. Zhang et al. [69] tested the extraction and separation of toluene and cyclohexane with a hollow fibre supported liquid membrane, impregnated with the ionic liquid N-butylpyridinium tetrafluoroborate ([BPy][BF_4]) or 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]). The removal efficiency was in a lower range between 37.47 to 42.59 %, but the membrane stability showed good long-term stability over 100 h. Zhang et al. [69] employed a resistance-in-series model to determine the dominant mass transfer resistance. The membrane phase resistance was the domi-

nant resistance, accounting for 98 and 87 % of the total resistance at 298 and 323 K, respectively. The OMTC was calculated to be 9.37 10^{-9} and 3.30 10^{-8} at 298 and 323 K, respectively. No validation was performed with experimental and simulated MTC-values.

Another possibility is the modelling of rare earth elements extraction procedures, which was performed by Jagdale et al. [70] and Martínez et al. [71]. Jagdale et al. [70] studied the effect of cations (H(I) and Na(I)) on the transport of Nd(III)-ions through hollow fibre contactors, impregnated with N, N, N′, N′-tetraoctyl-diglycolamide (TODGA), diluted with n-dodecane. A maximum extraction efficiency of 88.3 % was reached at equimolar concentrations of HNO_3 and $NaNO_3$ in the feed solution. A mathematical model based on the resistance-in-series approach was proposed to simulate the extraction process. The OMTC was determined by estimation of the equilibrium constant of the metal complexation reaction, the mass transfer coefficients at the feed and stripping side and the molecular diffusion coefficient, by employing different correlations. Whilst the model gave satisfactory predictions at a feed molarity of 3 M, it did not provide good agreement with the experimental data at a molarity of 2 M. This was most likely due to significant HNO_3-transport from the feed to the strip side. Martínez et al. [71] looked at the separation selectivity of a ternary mixture (yttrium, neodymium and dysprosium), using bis-(2-ethylhexyl) hydrogen phosphate (D2EHPA) as the extractant in a flat sheet SLM-setup. A transient model for an SLM-setup working batch-wise was developed to study the effect of different process parameters (agitation rate, feed and strip pH, extractant concentration and initial feed concentration) on the selectivity and process time. Qualitative effects of the process parameters were analysed by the authors, but to obtain a more quantitative simulation tool, more experimental data are needed.

Hydro-metallurgical extractions of metal ions and semi-metals was investigated by Willersinn and Bart [72] and Muhammad et al. [73]. Willersinn and Bart [72]

tested the extraction of Ge(IV) from aqueous solutions by two extractants, namely LIX 63 and Kelex 100, which refer to 5,8-diethyl-7-hydroxydodecan-6-oxime and 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline, respectively. A membrane-based, non-dispersive microcontactor was used for the extraction process. The used apparatus allows the study of solvent extraction kinetics at very low sample volumes, which is necessary for high-cost extractants. An adapted F-method was applied to calculate the mass fluxes, which solely incorporated the chemical reaction, as opposed to the diffusional parts. Validation of the predicted extraction kinetics for different residence times and extractants showed satisfactory agreement between the experimental and simulated data. In a study by Muhammad et al. [73], the extraction performance of Cu(II)-ions was investigated in two commercial hollow fibre membrane contactors X-40 and X-50, using trifluoro-acetylacetone (TFA) as the extractant. A resistance-in-series model was used to estimate the effect of various process parameters, such as flow rates and module geometry, on extraction efficiency and solute fluxes. An extraction efficiency of 78 % was reached in the X-40-module, whilst this value was equal to 20 % in the X-50-module, under the same hydrodynamic conditions.

From the applications mentioned above, it is clear that resistance-in-series models provide useful tools to determine performance characteristics (efficiency, solute fluxes, etc.) of different extraction applications. Next to conventional MBSE and SLM-applications, these models can also be applied to systems, employing dispersive feed or strip solutions. By calculation of the dominant mass transfer resistance, different countermeasures can be proposed to enhance mass transfer and efficiency of the considered system. Whilst the current literature focuses on lab-scale extraction applications, it may be an interesting strategy to focus on the transition to pilot-scale and full industrial applications. A study by Mans et al. [74] looked at the conceptual design of a cobalt-nickel refinery. Next to the determination of extraction isotherms and mass transfer behaviour, a comprehensive set of models was

applied to conceptually design an industrial cobalt-nickel extraction refinery for pregnant leach solutions from an industrial plant. This study showed the possible use of resistance-in-series models for upscaling of lab-scale equipment.

3.2 Computational fluid dynamics (CFD)

Apart from the resistance-in-series-model, computational fluid dynamics (CFD) can be employed to determine the hydrodynamics of a certain system, which influence the mass transfer behaviour through membranes. CFD is an emerging field in fluid mechanics, in which fluid flow and heat transfer problems are solved and analyzed using numerical algorithms and computational methods. CFD is most often used when a computational solution is faster, more cost-effective or more convenient. For example, if different parameters need to be varied, CFD may be useful to reduce the number of required experiments, leading to lower costs and less time spent on experimentation [75, 76]. Nowadays, detailed computational information about flows can be obtained at a fraction of the cost of the corresponding experiments, since computational resources have increased substantially at sharply decreasing costs. Therefore, CFD has become a powerful tool for research and development in multiphase flow systems [77].

CFD problems usually involve three stages. First, the computational domain of the problem is defined in the pre-processing stage. A mesh is generated by dividing the volume into smaller units or cells and the fluid flow is modelled using a mathematical model particular to the problem. More specifically, CFD is governed by differential equations, such as the Navier-Stokes system of equations, which is fundamental for fluid dynamics. Initial and boundary conditions are defined depending on the constraints. Secondly, the problem is solved numerically [75, 76]. The finite element method (FEM) is an important method to numerically solve differential equations. The concept of FEM is based on splitting the computational

domain into small patches, after which local solutions are calculated that satisfy the differential equation within the boundary of this patch. By combining the individual solutions on these patches, a global solution can be obtained. FEM is a flexible method, which can be adapted to a wide range of numerical problems, making it a universal tool for solving differential equations numerically [78]. The solution may be obtained iteratively, for steady-state solutions, whilst for time-dependent problems, the solution is found by numerically solving the equations for each time step. Lastly, the CFD results are analyzed by comparison with existing experimental results for validation [76].

Tables 4 and 5 give some key examples of CFD-based studies of membrane-based extraction processes, showing the wide variety of CFD-modelling applications. FEM seems to be the method of choice for the numerical solution of the considered systems, which was a single or multi-hollow fibre module. The group of Ghadiri published a significant amount of papers on the topic of CFD in MBSE- and SLM-applications. The studied applications ranged from removal of organics [79, 80, 81] to the recovery of metal ions [82, 83]. Other groups have also investigated CFD for the simulation of organics extraction [84, 85, 86] and recovery of copper [87], uranium [88, 89], vanillin [90] and pharmaceuticals [91, 92].

From the above-mentioned papers, it is clear that CFD can be used for a wide range of industrial applications. It enables the simulation of hydrodynamics in membrane contactors (in an MBSE- or SLM-configuration), providing the tools to determine mass transfer behaviour and performance characteristics of a certain separation case. The use of CFD enables the analysis of velocity, concentration and pressure profiles. Magalhães et al. [85] studied the flow behaviour inside a separation module, which provided insight in the fluid dynamics inside of the device. For increased turbulence, a higher solute concentration was obtained, reducing the concentration polarization effect. A study by Muhammad et al. [87] simulated the solute concentration profile in three sections of a hollow fibre membrane contac-

tor. They found that a decreased feed flow rate and increased partition coefficient led to a higher diffusive flux in radial direction. Furthermore, extraction efficiency increased from 75 to 95 % at higher temperatures. However, no validation was performed of the hydrodynamics for both studies. Next to the velocity profiles, CFD also allows to determine the effects of process parameters on the extraction performance. Hemmati et al. [84] found that an increased feed flow rate enhanced the extraction efficiency of phenol, whilst the solvent phase flow did not change the performance. Therefore, CFD enables a fast manner to model extraction performance for varying process conditions. Whilst confidence in CFD is growing, corroboration of the simulated results with experimental or analytical results is still needed, which states the need for comparative experiments [76]. Furthermore, CFD uses a number of assumptions (e.g. constant solvent viscosity and density, constant solute diffusion coefficient, and incompressible, isothermal and steady-state flow), which might not be valid for all industrial cases [85]. Another challenge in CFD is the validation of the obtained velocity and concentration profiles, since local measurements of these profiles cannot be obtained experimentally [88, 89]. Next to CFD, other techniques can be used as well to simulate the extraction behaviour. An example is the study by Michel et al. [93], in which an artificial neural network was used for the prediction of extraction efficiency in a supported liquid membrane. The results were in good agreement with the experimental data, with average deviations of less than 3 %. However, CFD remains the main go-to tool for simulation of extractive operations, employing membranes.

Table 1: Characteristics of resistance-in-series modelling of membrane-based extraction processes.

No.	Application	Membranes and configuration	Results	Ref.
1	Uranium recovery from nuclear waste	Use of a hollow fibre polypropylene membrane contactor with strip dispersion	Estimation of mass transfer coefficients via a resistance-in-series model; a good agreement was obtained between the experimental and modelled MTCs, which were 2.174 $10^{-}2$ and 2.49 $10^{-}2$ cm/s, respectively	[63]
2	Cephalexin recovery from aqueous solutions by Aliquat 336	Use of a hollow fibre membrane contactor with dispersed organic droplets in the feed	Determination of mass transfer resistances using the resistance-in-series approach; the model showed good agreement between the experimental and theoretical MTCs with a relative error of less than 15 %, for varying carrier concentrations; the overall mass transfer coefficient increased with a higher organic-to-feed volume ratio and a lower initial feed concentration	[67]
3	Phenol extraction and stripping by trioctylphosphine oxide	Use of a hollow fibre polypropylene membrane contactor in an SLM-configuration	Development of a kinetics model using the resistance-in-series approach; simulation of the effects of feed phenol concentrations and flow rates on extraction performance; the model showed excellent correlation between the experimental and simulated results	[68]

Table 2: Table 1 continued.

No.	Application	Membranes and configuration	Results	Ref.
4	Toluene and cyclohexane separation by membrane extraction	Use of a hollow fibre supported ionic liquid membrane contactor	Mass transfer resistance determination by using the resistance-in-series approach; the membrane phase resistance was 9.37 $10^{-}9$ and 3.30 $10^{-}8$, accounting for 98 and 87 % of the total resistance, at 298 and 323 K, respectively	[69]
5	Metal ion extraction, namely Nd(III)	Use of a hollow fibre, supported liquid membrane contactor operated in a recycling mode	Use of a resistance-in-series approach for modelling of extraction efficiencies and concentration profiles; the model gave satisfactory results for a feed of 3 M HNO_3, but failed for a lower feed acidity	[70]
6	Rare earth elements, namely yttrium, neodymium and dysprosium, separation from aqueous streams by D2EHPA (di(2-ethylhexyl)phosphoric acid)	Use of a flat sheet supported liquid membrane	Mass transfer modelling by using the resistance-in-series approach to determine the influence of initial feed concentration, agitation rate, stripping pH and extractant concentration on the selectivity	[71]
7	Ge(IV)-extraction from aqueous solutions by LIX 63 and Kelex 100 in kerosene	Use of a membrane-based microcontactor	Mass transfer modelling by using the resistance-in-series approach; effective germanium extraction was only possible in harsh conditions, namely high extractant concentrations and high acidities	[72]

Table 3: Table 2 continued.

No.	Application	Membranes and configuration	Results	Ref.
8	Cu(II)-extraction from aqueous solutions by TFA dissolved in 1-decanol	Use of hollow fibre membrane contactors X-40 and X-50 with hydrophobic, polypropylene fibres	Mass transfer modelling by using the resistance-in-series approach for the determination of solute efficiency, transmembrane flux and height of the transfer unit for two distinct membrane modules; up to 78 % of extraction efficiency for the X-50 module	[73]
9	Cobalt-nickel extraction from pregnant leach solutions	Use of a hollow fibre membrane contactor	Mass transfer modelling by using the resistance-in-series approach; a conceptual design of 6 membrane contactor modules was proposed, reaching a Ni-raffinate of 99.99 % purity	[74]
10	Ammonium nitrogen recovery from human urine	Use of an open-loop hollow fibre polypropylene membrane contactor	Mass transfer modelling by using the resistance-in-series approach; the ammonia capture efficiency dropped from 80.13 to around 30 %, if the feed flow rate increased; a higher feed pH increased the efficiency	[94]

Table 4: Characteristics of CFD-based modelling of membrane-based extraction processes. The validation and accuracy of the simulations were mentioned, if available

No.	Application	Membranes and configuration	Results	Ref.
1	Organics removal from aqueous (waste) streams	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations of extraction performance using FEM; validation through comparison with experimental extraction data showed good agreement (average deviation = 10 % [80])	[79, 80]
4	Reactive extraction of benzoic acid from aqueous waste streams by TOA (trioctylamine) dissolved in 1-octanol	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations using FEM for the determination of benzoic acid transport; an increased feed flow rate decreases the benzoic acid removal efficiency; validation through comparison with experimental reactive extraction data (average deviation = 4 %)	[81]
2	Metal ion extraction from aqueous solutions by varying extractants	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations using FEM for the determination of concentration, velocity and pressure profiles; validation through comparison with experimental extraction data showed excellent agreement	[82, 83]

Table 5: Table 4 continued.

No.	Application	Membranes and configuration	Results	Ref.
3	Phenol removal from aqueous waste streams	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations for the determination of concentration and velocity distribution in the membrane contactor; a higher feed flow rate reduces the phenol extraction efficiency; validation through comparison with experimental extraction data (< 15 % error)	[84]
5	Oil and grease removal from aqueous industrial effluents	Use of a ceramic membrane contactor	CFD-simulations using FEM for the determination of streamlines and velocity, pressure and concentration fields; the polarization layer effect was reduced by enhancing turbulence and the insertion of an impermeable section into the inlet of the contactor; no validation was performed	[85]
6	Extraction of aroma compounds, namely dimethyltrisulfide (DMTS), ethyl butyrate (EB), benzaldehyde (BA) and 2-phenyl ethanol (PE), from aqueous streams by hexane	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations using FEM for the determination of solutes' concentration; validation through comparison with experimental extraction data showed excellent and good agreement, for DMTS and EB, respectively; more deviation was observed for BA, due to experimental error or lack of precision; standard error = 0.2 for PE	[86]

Table 6: Table 5 continued.

No.	Application	Membranes and configuration	Results	Ref.
7	Cu(II)-extraction from aqueous solutions by TFA (tri-fluoro-acetylacetone) dissolved in 1-decanol	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations using FEM for the determination of the influence of membrane characteristics, partition coefficient and flow configuration on extraction efficiency; no validation was performed	[87]
8	Uranium extraction from aqueous HNO_3-solutions by TBP in *n*-dodecane	Use of a hollow-fibre polypropylene membrane contactor	CFD-simulations for the determination of hydrodynamics and mass transfer; validation through comparison with experimental extraction data showed good agreement	[88, 89]
9	Extraction of vanillin or penicillin G from aqueous solutions	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations for the determination of hydrodynamics and mass transfer; study of the effect of solvent type, flow rates and membrane design; validation through comparison with experimental extraction data showed good agreement	[90, 91]
10	Removal of ibuprofen from aqueous aqueous waste streams	Use of hollow fibre membrane contactors with hydrophobic, polypropylene fibres	CFD-simulations for the determination of hydrodynamics and mass transfer; study of the effect of membrane design on performance; validation through comparison with experimental extraction data (MSE = 1.42 - 7.29 10^3)	[92]

4 APPLICATIONS OF MEMBRANE-BASED LIQUID-LIQUID EXTRACTION

Different configurations are used for membrane applications, namely flat sheet, tubular and hollow-fibre membranes [95]. For membrane extraction applications, contactors with flat sheet as well as cylindrical walls may be used. However, only hollow fibre modules are available commercially in cylindrical contactors [16]. This section gives an overview of the different membrane-based extraction technologies. Both membrane-based solvent extraction (MBSE) and supported liquid membrane extraction (SLME) applications are described. For an overview of bulk and emulsion liquid membrane technology, the reviews by Kumar et al. [24] and Chang [96] can be consulted.

4.1 Membrane-based solvent extraction (MBSE)

The possibility to use membrane-based solvent extraction in industrial applications is investigated in many studies. Its technology is applicable to a wide variety of industries, such as metallurgical and mining, chemical and biochemical industries. Wastewater treatment is another option, benefiting from the use of MBSE, as well as the recovery of rare earth elements from defined waste streams. The following discussion includes the comparison of different MBSE-applications, related to fluxes and extraction performance. An overview of the research on this subject after 2013 is given in Tables 7 up to 13. For previous works, the reviews by Pabby and Sastre [2] and Gabelman and Hwang [26] can be consulted.

4.1.1 Metal recovery

A first important MBSE-application is metal recovery. Yeh et al. [97] studied the selective separation of Co(II) from Ni(II) in a sulfate solution, by using a hollow fibre extractor and stripper. Cyanex 302 dissolved in kerosene was used as the extractant, whilst the strippant was a sulphuric acid solution. An increase of the feed pH and Cyanex 302 concentration led to higher extraction rates of both metals, but Co(II) was preferentially extracted. Co(II)-recovery increased further with increasing strip acidity and strip flow rate, making it a good alternative for conventional extractive separation processes, such as chemical precipitation and oxidation. Another study by Mans et al. [74] developed a methodology to design an extraction column for the purification of a pregnant leach solution, containing Co(II) and Ni(II). The final proposed design resulted in an industrial setup of six hollow fibre, polypropylene membrane modules, with Cyanex 272 dissolved in Shellsol D70 as the extractant. The setup enabled a raffinate purity of 99.99 % Ni(II). Song et al. [98] tested the use of a flat sheet, PES/SPPESK membrane for the selective separation of Cu(II) from Ni(II), with LIX84-I/dodecane as the extractant and a sulphuric acid solution as the strippant. A complete separation of Cu(II) from Ni(II) was achieved by adjusting the feed pH to 2.9. The use of a sandwiched membrane contactor in which two membranes separate the extractant from the feed and strippant, showed higher Cu(II)-fluxes, whilst the membrane exhibited a good stability during 30 days.

A study by Laso et al. [99] compared the use of MBSE and emulsion pertraction technology (EPT) for the selective separation of Zn(II) over Fe(II) from spent pickling wastes. Tributylphosphate (TBP) and water were used as the extractant and strippant, respectively. Although the EPT process showed better separation kinetics, MBSE had a higher selectivity. Further research should investigate the maximum allowable pH and Cl^-- and Fe(II)-concentration for conducting Zn(II)-recovery by electro-deposition. San Román et al. [100] proposed a flowsheet for the selective

recovery of Fe(II) from a hydrochloric acid solution with Zn(II) via an MBSE-setup and a consecutive electrodialysis step for acid removal. The recovered Fe(II)- and Zn(II)-solutions may then be further processed to obtain valuable products, such as metallic zinc and $FeCl_3$.

The removal of Li(I)-ions from aqueous streams has been investigated in many studies. Since membrane stability has been a key issue for liquid-liquid membrane extraction, Xing et al. [31] introduced the use of a new type of solvent resistant material, namely poly(ethylene-co-vinyl alcohol) (EVAL). For an MBSE-test, using TBP dissolved in kerosene as the extractant, the Li(I)-flux was proportional to the feed concentration. Furthermore, long term stability tests showed a stable Li(I)-flux for about 43 days, indicating the potential of EVAL for Li(I)-extraction purposes. In another study, Huang et al. [101] proposed the use of poly(ether-ether-ketone) (PEEK) membranes for the stripping step in Li(I)-extraction, due to the use of a highly acidic HCl-strippant. The PEEK membrane remained stable for 21 days. An extraction-stripping close-loop is then available by using EVAL- and PEEK-membranes in the extraction and stripping steps, respectively. In a follow-up study by Huang et al. [102], they investigated the effect of ethylene content on EVAL membrane morphology and performance. For increased ethylene content, the membrane had a smaller pore size and increased mechanical strength, but a reduced water flux and ion permeability. This work provided a theoretical methodology for controlling the membrane morphology in Li(I)-extraction. To reduce the ion diffusion resistance in the PEEK membrane, Huang et al. [32] blended PEEK with sulfonated PEEK (SPEEK) and tested their performance. A 50/50 PEEK/SPEEK membrane showed the highest water permeability and Li(I)-fluxes, which was about two times the extraction flux and five times the stripping flux, compared to the PEEK membrane. Lastly, a study by Zhang et al. [94] checked the use of blended EVAL/SPEEK-membranes for membrane extraction of Li(I). Only a small increase in SPEEK-content was sufficient to increase the Li(I)-flux, but further increase led to a highly compact skin layer, re-

ducing the effect. The extraction flux of this membrane was higher than any other flux found in literature, using the same characterization method. MBSE can also be used for bromine recovery. Zhang et al. [103] tested the recovery of bromine by contacting an aqueous brine solution with an aqueous NaOH-solution, separated by hollow fibre, PVDF membranes. The key parameters for the extraction were the feed flow rate, feed concentration and temperature. A mathematical model was used to predict the bromine recovery behaviour.

As presented in this section, MBSE can be used for the recovery of different metals, such as cobalt, nickel, iron, zinc, etc. Optimization of the process parameters, such as feed and strippant pH, flow rates, etc., further increases the observed extraction rates. By developing solvent resistant materials, such as EVAL, PEEK and blended membranes, the performance related to membrane stability and transport properties is increased. By employing blended membranes (EVAL/SPEEK) for Li(I)-extraction, the extraction flux was higher than any other experimental flux available in literature, signifying its performance. Next to hollow fibre modules, other designs, such as a sandwiched membrane contactor, were developed. Even pilot plant setups and hybrids of MBSE and other separation technologies were designed, showing its industrial potential.

4.1.2 Rare earth element recovery

The separation of precious ions, namely rare earth elements, is the focus of a number of studies. Rare earth elements are used in many electronic and electromagnetic devices, and can be recovered from waste streams of these devices. Duhamet et al. [104] tested the recovery of neodymium from aqueous nitric acid streams into the extractant bis(2-ethylhexyl) phosphate (HDEHP) dissolved in the oil Isane IP 175. A cylindrical, polypropylene membrane contactor was used in the setup. According to their study, the separation requires the use of specific ion binding extractants in high concentrations. If the ion concentration is too high, these extractants tend to

form a blocking or fouling layer, reducing the transmembrane flux. Relevant parameters are the membrane structure, thickness and wettability and the type of oil and extractant. Touré et al. [105] also tested neodymium extraction in a hollow fibre, polypropylene membrane, with different extractants, namely *N*,*N*-dibutylacetamide (DBAc) and HDEHP. For DBAc, the neodymium mass transfer showed a high resistance, due to a low distribution coefficient, leading to decreased membrane diffusion. When HDEHP in *n*-dodecane was used as the extractant, the distribution coefficient of Nd was three times higher. It was observed that the neodymium mass transfer rates depend on the distribution and diffusion coefficients.

These studies show that in industrial applications, it is important to select a suitable extractant, giving a high distribution coefficient. Furthermore, the third phase or blocking layer, formed by the extractants, should be avoided, by either destroying the phase mechanically or by decreasing the ion concentration, hence increasing the ion flux.

4.1.3 Wastewater treatment

Phenol is a common organic water pollutant, because it is an important raw material in various industries. Traditionally, it is removed by oxidation, adsorption or liquid-liquid extraction. Hasanoğlu [106] investigated the use of pertraction technology for phenol removal. They compared gas-filled membrane, solvent and emulsion membrane applications. An aqueous feed stream with phenol was separated from a NaOH-solution by a polypropylene membrane, impregnated with 1-decanol. The ELM process showed the highest promise, in terms of recovery and phenol removal, mainly because the stripping step was limiting to the MBSE-process. This could be improved by using multiple stripping modules in series. Xiao et al. [107] described the pertraction properties of phenol through a composite PDMS/PVDF membrane, compared to a silicone rubber membrane. The authors reported overall mass transfer coefficients (OMTC) 5 to 10 times higher than reported previously in

literature for a non-composite PDMS membrane. However, the authors also note that temperature effects and feed flow rates significantly influenced the mass transfer coefficients. Therefore, process parameters during the extraction procedure play an important role in the final extraction performance and mass transfer rates.

Organic acids are also important wastewater contaminants. An example is benzoic acid, which is present in effluents of food industries. It is mainly removed by adsorption and catalytic degradation, but a hollow fibre, polypropylene membrane contactor was proposed as an alternative by Agrahari et al. [108]. An aqueous benzoic acid solution was contacted with trioctylamine (TOA) dissolved in 1-octanol, resulting in a BA-removal of more than 95 %. A further study is needed to investigate extractant regeneration and to optimize the used solvent to treated water ratio. Kong et al. [109] published a paper concerning the removal of *p*-toluic acid (PT) from purified terephthalic acid (PTA) wastewater, which is a feedstock for the polyester industry. A hollow fibre, polypropylene MBSE-method was employed, using *p*-xylene as the extractant, resulting in residual PT-concentrations of less than 100 g/m^3 after 60 s. An optimization of the process parameters (operating time, temperature, etc.) was performed and suggested values were given for an industrial design. In a follow-up study, Kong et al. [110] proposed the use of a helical, polypropylene hollow fibre module. The experiments showed that the extraction efficiency was doubled compared with the straight hollow fibre. This is mainly due to Dean vortices, which convey the peripheral fluid to the centre, and vice versa, leading to enhanced mass transfer.

The purification of wastewater could also lead to its use in other industries. Licon Bernal et al. [111] investigated the removal of ammonium from wastewater treatment plant effluents to allow for its use in a hydrogen production plant. A polypropylene, hollow fibre membrane contactor was used with an aqueous sulphuric acid solution as the stripping solution. Suitable levels of ammonium removal were achieved down to 1 mg/L through appropriate pH control. The removal ef-

ficiency was improved by raising the pH or the flow rate. Apart from wastewater treatment, MBSE can be used for other purification purposes. Biodiesel engines require a high purity fuel, which is normally achieved by removal of a large amount of water and multiple distillation steps. Amelio et al. [112] tested the use of an MBSE-contactor for removal of the impurities, methanol and glycerol, from a synthetic biodiesel stream, consisting of rapeseed oil and methyl esters. A PTFE, flat sheet module was used, with water as the extractant, and it showed its potential for biodiesel purification. The membrane did show fouling, after usage in the membrane module, which was linked to a reduction of the membrane hydrophobicity. However, further investigations are required for the final industrial design, regarding the effect of temperature, pore size, solvent type, etc.

Whilst traditional separation methods, such as oxidation and adsorption, are mainly used in industry, MBSE is a promising alternative for wastewater treatment. An industrial MBSE-design was proposed for *p*-toluic acid removal from wastewater by Kong et al. [109]. The removal of other contaminants, such as phenol and benzoic acid, via MBSE still requires process redesign and optimization. Additionally, some studies proposed the use of MBSE for wastewater purification, which enables its use in other industries, such as hydrogen production. In these studies, suitable extraction efficiencies were achieved for industrial implementation.

4.1.4 Membrane extraction for the nuclear industry

Membrane extraction can also present possibilities for separation processes in the nuclear industry. An example is the development of effective methods for uranium extraction from low-grade ores for the production of U_3O_8. Biełuszka et al. [113] implemented a membrane contactor for the processing of post-leaching liquors to separate uranyl ions. As an extractant, di(2-ethylhexyl)phosphoric acid (D2EHPA) was found to be most favourable. The resulting high extraction levels enable this method to be an alternative compared to the conventional mixer-settler configu-

ration. Next to uranium, zirconium (Zr) is an important element in the nuclear industry, since it is used as a cladding material for nuclear reactors. To obtain nuclear grade Zr, its hafnium (Hf) concentration needs to be less than 100 mg/dm^3. Apart from ion exchange and distillation, membrane extraction is investigated as an alternative by Conradie et al. [114] for different extractants and strippants. More specifically, DiOPA, Ionquest 801 and D2EHPA were used as the extractants and $(NH_4)_2CO_3$, $CaCl_2$, H_2SO_4 and $C_2H_2O_4$ as the strippants. The MBSE-experiment showed that extraction using D2EHPA increased the Zr purity from 97.2 % to 99.0 % in a single contact stage. $CaCl_2$ gave the highest stripping selectivity, maintaining a Zr purity of 99.0 %, whilst $C_2H_2O_4$ gave the highest zirconium yield in the strippant. Meerholz et al. [115] designed an automated MBSE-system for selective separation of Zr and Hf, in which the flow rate and pressure were controlled to improve accuracy and repeatability of the extraction results. This system could then be used for further concept-of-proof studies to get highly reproducible extraction results.

4.1.5 Recovery of organic compounds

Organics recovery is another possibility for the use of MBSE. Burgé et al. [116] tested the use of reactive liquid-liquid extraction for the recovery of 3-hydroxy-propionic acid (3-HP) from bioconversion media of *Lactobacillus reuteri*. A polypropylene, hollow fibre contactor was used, with TOA and Aliquat 336 dissolved in *n*-decanol as extractants. The feed pH and concentration and extractant composition had the highest influence on the extraction performance. The setup showed a high selectivity and potential for use in the biotechnological industry. An important advantage of the use of a hollow fibre membrane contactor is that direct contact between the organic phase and microorganisms is avoided. The used extractants, TOA and Aliquat 336, have been described as potentially toxic for certain microorganisms. Another example is the recovery of volatile fatty acids (VFA), which can be used as precur-

sors for many products, such as solvents, inks, coatings, etc. Plácido and Zhang [117] tested two alternatives, namely esterification and MBSE, for the recovery of VFAs, produced by anaerobic mixed fermentation (AMF) of slaughterhouse blood. The MBSE-system, in which a TOA/octanol mixture was used as the extractant, showed a VFA-recovery of over 80 %, making it a suitable downstream process for the AMF-configuration. Apart from VFAs, alcohol recovery can be an interesting option for MBSE. Snochowska et al. [118] tested the use of a hollow fibre contactor for ethanol recovery with an ionic liquid [BMIM][$MeSO_4$] as the extractant. Extraction efficiencies of up to 20 % were achieved, for low ethanol concentrations in the feed, but the efficiency dropped for higher feed concentrations. Terpenes are another organic compound, which occur naturally in plant cells, and can be used by flavour and fragrance industries, as well as pharmaceutical applications. Janoschek et al. [119] simulated the removal of two monoterpenes, (S)-(+)-carvone and terpinen-4-ol, *in silico*, to select the most suitable solvents. The carvone removal was then tested in a PTFE, hollow fibre contactor, with *n*-heptane as the solvent, due to its lower toxicity and high partition coefficient. A nearly complete carvone extraction was achieved within 8 hours of process time, when the feed flowed through the fibre lumen, whilst a higher extraction efficiency was reached for the opposite case. The technology is thus applicable to industrial product removal.

Table 7: Membrane-based extraction processes used for different industries. The number in the first column indicates the industrial branch: metallurgical and mining industry (1), wastewater treatment (2), organics industry (3), petroleum and fuel industry (4), rare earth elements (5), other industries (6).

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
1	Aqueous HCl-solution of Li(I), Mg(II), etc.	$NaFeCl_4 \cdot TBP_{(O)}$ in kerosene	N/A	Flat sheet EVAL membrane; a Li(I)-flux of 2.7 10^{-8} mol/($cm^2 \cdot s$) was achieved at a feed concentration of 0.1 M; EVAL membranes are promising barriers for Li(I)-extractions, due to long-term stability of the Li(I)-flux and controllability of membrane morphology	[31]
1	Aqueous solution of Li(I) and Mg(II)	$NaFeCl_4 \cdot TBP$ in kerosene	Aqueous HCl-solution	Flat sheet PEEK/SPEEK membrane; a 50/50 blended PEEK/SPEEK membrane showed five times higher Li(I)-extraction fluxes and two times higher Li(I)-stripping fluxes, compared to the PEEK membrane	[32]
1	Pregnant leach solution (Ni(II), Co(II), etc.)	Cyanex 272 in Shellsol D70	N/A	Hollow fibre polypropylene membrane; Co(II)- and Ni(II)-recoveries of over 90 and less than 10 % were reached in the setup, enabling a selective extraction	[74]
1	Aqueous solution of Mg(II) and Li(I)	$NaFeCl_4 \cdot TBP_{(O)}$ in kerosene	N/A	Flat sheet EVAL and EVAL/SPEEK membranes; a non-woven EVAL/SPEEK membrane showed a Li(I)-extraction flux of 4.80 10^{-8} mol/(cm^2s), which two times the flux of the EVAL-membrane	[94]

Table 8: Table 7 continued.

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
1	Aqueous sulfate solution of Co(II) and Ni(II)	Na-Cyanex 302 in kerosene	Aqueous H_2SO_4-solution	Hollow fibre polypropylene membranes; the highest Co(II)-extraction and stripping efficiencies, 84.6 and 43.7 %, were reached in the one-stage hollow-fibre experiments	[97]
1	Aqueous solution of Cu(II) and Ni(II)	LIX84-I and dodecane	Aqueous H_2SO_4-solution	Single-stage and sandwiched flat sheet, PES/SPPESK blend membrane; the average Cu(II)-flux increased from 4.20 10^{-9} to 5.6 10^{-9} mol/(cm^{2}s) if the sandwiched module was used; the use of a low feed pH further enhanced copper fluxes and selectivity; the used membranes are stable for 30 days and prevent extractant loss	[98]
1	Aqueous HCl-solution of Zn(II) and Fe(II)	TBP and Shellsol D70	Tap water	Hollow fibre polypropylene membranes; Zn(II)- and Fe(II)-extraction efficiencies of 80 and 15 % were reached in the ME-setup, whilst these values were 79 and 30 % in the ELM-case; ME shows higher selectivity, but slower kinetics; efficiency increase by optimizing TBP-content and phase ratio	[99]

Table 9: Table 8 continued.

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
1	Aqueous HCl-solution with Fe(II) and Zn(II)	Pure TBP	Service water	Hollow fibre, microporous membranes; Fe(II)-, Zn(II) and HCl-recoveries of 60, 70 and 10 % were reached in the MBSE-setup after 1 h; combination with electrodialysis is and alternative for HCl- and metal recovery	[100]
2	Aqueous solution of Li(I)	TBP and kerosene	Aqueous HCl-solution	Flat sheet, PEEK and EVAL membranes; increased PEEK content decreases water permeability and diffusino flux; EVAL and PEEK membranes may be used for extraction and stripping purposes, respectively; PEEK membrane stability of 504 h was reached	[101]
2	Aqueous solution of Li(I)	TBP and kerosene	Aqueous HCl-solution	Flat sheet EVAL membranes; increased ethylene content in EVAL membranes improved mechanical strength, but reduced water flux and ion permeability; high EVAL-crystallinity lead to a 50 % reduction in Li(I)-permeance	[102]
1	Aqueous bromine solution	Aqueous NaOH-solution	N/A	Hollow fibre, PVDF membranes; a maximum K_{ov}-value of 9.0 10^{-6} m/s was reached; this value was positively influenced by an increased feed flow rate and temperature	[103]

Table 10: Table 9 continued.

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
5	Aqueous HNO_3-solution of Nd(III)	Bis(2-ethylhexyl) phosphate and Isane IP 175	N/A	Tubular polypropylene membrane; the Nd-distribution coefficient K_D drops from 130 to 20 for an increased feed Nd-concentration from 0.05 to 0.5 g/L; the ions and ligands form a blocking layer on the membrane at high concentrations, limiting rare earth element extraction rates	[104]
5	Aqueous HNO_3-solution of Nd, Dy and Pr	DBAc or HDEHP in *n*-dodecane	Water or aqueous HNO_3-solution	Hollow fibre polypropylene membrane; Nd-recoveries of over 90 and 95 % were reached for solvents DBAc and HDEHP, respectively	[105]
2	Aqueous phenol solution	1-decanol	Aqueous NaOH-solution	Hollow fibre, polypropylene membrane; ELM shows more promise than MBSE for phenol removal with extraction and stripping efficiencies of 99.4 and 84.6 % and a K_{ov} of 1.48 10^{-6} m/s	[106]
2	Aqueous phenol solution	N/A	Aqueous NaOH-solution	Flat sheet, PDMS/PVDF and silicone membrane; a five times higher K_{ov}-value (15.0 10^{-7} m/s) was reached for the composite membrane, compared to the silicone one	[107]

Table 11: Table 10 continued.

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
2	Aqueous solution of benzoic acid	TOA in 1-octanol	N/A	Hollow fibre polypropylene membrane; benzoic acid extraction efficiencies of up to 95 % were achieved	[108]
2	*p*-toluic acid and water in purified terephthalic acid wastewater	*p*-xylene	N/A	Hollow fibre polypropylene membrane; satisfactory extraction efficiencies up to 91 % was reached with extraction times longer than 60 s; process optimization by model simulation	[109]
2	Aqueous solution of purified terephthalic acid	*p*-xylene	N/A	Helical hollow fibre polypropylene membrane; use of a helical HF doubles the extraction efficiency compared to a straight HF; process optimization by model simulation decreases the required extraction time from 50 to 27 s, compared to the straight HF	[110]
2	Aqueous solution of ammonium	Aqueous H_2SO_4-solution	N/A	Hollow fibre polypropylene membrane; a suitable ammonia concentration reduction was achieved from 15 to 1 mg/L; the extraction efficiency increased for increased pH or flow rates; a buffer solution was needed in the working solution to achieve the requirements	[111]

Table 12: Table 11 continued.

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
4	Methyl esters, rapeseed oil, methanol and glycerol	Water	N/A	Flat sheet PES, PP, PVDF and PTFE membrane; a maximum K_{ov}-value of 1.5 10^{-6} m/s was reached; effect of solutes concentration and flow rates on the fluxes	[112]
1	Aqueous H_2SO_4-solution of uranyl nitrate	D2EHPA in kerosene or toluene	Aqueous Na_2CO_3- or $(NH_4)_2CO_3$-solution	Hollow fibre polypropylene membrane; D2EHPA is a favourable extraction agent, attaining high uranium extraction and stripping efficiencies up to 98.20 and 97.77 %	[113]
1	Aqueous H_2SO_4-solution of Hf(IV) and Zr(IV)	D2EHPA in cyclohexane	Aqueous $CaCl_2$- or $C_2H_2O_4$-solution	Hollow fibre, hydrophobic membranes; a Hf- and Zr-extraction efficiency of 72 % and 44 % was reached, with 28 % Hf-selectivity; $CaCl_2$ was the most selective stripping agent	[114]
1	Aqueous solution of Hf(IV) and Zr(IV)	Cyanex 301 in cyclohexane/ 1-octanol	N/A	Hollow fibre PTFE membrane; use of an automated system for flow rate and pressure control during extraction led to highly reproducible extraction results with standard deviations varying by less than 1.2 %	[115]

Table 13: Table 12 continued.

No.	Donor phase	Acceptor phase	Stripping phase	Configuration, used membranes and results	Ref.
3	Aqueous solution with 3-HP	TOA and Aliquat 336 in *n*-decanol	N/A	Hollow-fibre, polypropylene membrane; the highest extraction efficiency (94.7 %) was reached with a mixture of 10 % Aliquat 336 and 10 % TOA in *n*-decanol, at a low aqueous phase pH and low 3-HP-concentrations	[116]
6	Aqueous solution with different organic acids	Octanol and TOA	N/A	Hollow fibre, polypropylene membrane; comparison of esterification and MBSE for VFA-recovery from slaughterhouse blood; the MBSE-system achieved the highest VFA-recovery of more than 80 %, making it a suitable downstream process	[117]
3	Diluted aqueous solution of ethanol	1-butyl-3-methyl-imidazolium methyl sulfate	N/A	Hollow fibre polypropylene membrane; the use of ionic liquid extractant gives satisfactory extraction efficiencies of diluted samples (1 to 5 wt%)up to 20.18 %; ethanol concentrations of 17 to 30 wt% were reached in the extract	[118]
3	Aqueous solution of (S)-(+)-carvone	*n*-heptane	N/A	Hollow fibre PTFE membrane; partitioning simulation for non-polar solvent selection; an overall product recovery of over 90 % was reached	[119]

4.2 Supported liquid membrane extraction

Due to the inherent advantages of SLM-configuration, intensive research has been carried out on different SLM-applications. As stated before, a supported liquid membrane is a porous membrane, of which the pores are impregnated with the solvent. Typically, porous polymeric membranes are used as support format, which are filled with water immiscible, organic solvents [19]. Many studies have been published, discussing polymeric membrane extraction for a variety of applications, such as metal and rare earth elements recovery and treatment of wastewater and high level waste. This section includes the discussion of different SLM-applications, related to fluxes, cycle life and extraction performance. Especially, cycle life and stability strongly influence the economics of the considered system, which is linked to module degradation and replacement [2]. An overview of the research on this subject after 2013 is given in Tables 14 up to 33.

4.2.1 Metal recovery

The removal and selective separation of metal ions from hydrometallurgical process streams is an important technology, since it enables the recovery of valuable metals and diminishes environmental pollution problems. Many recovery techniques exist, such as precipitation and solvent extraction, but they usually require considerable energy use and large amounts of solvents. Therefore, membrane-based separations are proposed as an alternative, due to their low energy consumption and mild operating conditions. Supported liquid membranes received growing attention, due to their inherent advantages, such as the small volume required of the organic solvent and carrier and a high separation factor. The main challenge of the SLM technique, limiting its commercial potential, is its performance decay for longer operating times. The stability decay can be induced by to the loss of the membrane

phase by evaporation or dissolution into the other phases or the type of polymeric support or solvent [120].

A study by Peydayesh et al. [121] described the recovery of Cd(II) and Zn(II) using a PTFE membrane with different membrane carriers, namely D2EHPA, M2EHPA or Cyanex 302, dissolved in kerosene. It was found that a mixture of D2EHPA and M2EHPA was the most appropriate carrier for Cd(II)- and Zn(II)-extraction. M2EHPA is more soluble in water than D2EHPA and thus decreases the membrane stability, but TBP was used to enhance the stability. Mahmoodi et al. [122] described the selective separation of Cd(II) and Ni(II) by a PTFE membrane, impregnated with D2EHPA and MEHPA in kerosene, and sulphuric acid as the strippant. Cd(II) was extracted selectively from Ni(II), with extraction efficiencies of 83.3 % and 0.45 % for both ions, respectively. The performance of the membrane remained acceptable for two runs of 12 hours, whilst it decreased significantly after three runs. In another study by Duan et al. [123], the separation of Ni(II) from ammonia solutions by a PVDF membrane was studied. The membrane was impregnated with Acorga M5640 in kerosene. Almost all of the Ni(II) was extracted from the feed after 18 hours of operation. The SLM-stability was satisfactory for 84 hours or seven runs of the extraction experiment.

Another approach to improve SLM stability is the use of ionic liquids (ILs) as the membrane phase. ILs normally consist of an organic cation and an inorganic or organic anion and have properties (such as a very low vapor pressure) resulting in more stable membrane phases. De Los Ríos et al. [120] investigated the use of a flat sheet, supported ionic liquid membrane (SILM) for the selective separation of Fe(III), Zn(II), Cd(II) and Cu(II). The used ionic liquid was methyltrioctylammonium chloride. The membrane enabled the selective recovery of Fe(III), Zn(II) and Cd(II), if water, sodium carbonate or NH_3 were used as the stripping phase, respectively. Furthermore, the membrane showed a remarkable stability, even for varying feed pH and strippants. The percentage of IL lost varied between 10 to 25

%, even after 456 hours of operation. A study by Castillo et al. [124] investigated the use of quaternary ammonium- and phosphonium-based ionic liquids for Cu(II)-extraction from liquid mining waste containing sulfates or chlorides. Stability tests for different ILs indicated that a mixture of Aliquat 336 and Cyanex 272 had the best performance, with extraction efficiencies up to 95 %. Although Kim et al. [125] reported that membrane-based extraction systems typically do not experience fouling caused by an accumulation of particulate matter, Castillo et al. [124] observed a fouling problem after approximately 4 hours of testing, which decreased permeability. The stability of the liquid membrane was linked to the fouling behaviour, which was caused by precipitation of the carrier complex or separation of the ionic liquid layer in sulphate or chloride media. Only Aliquat 336 and Cyanex 272 showed stability in both sulphate en chloride media. Furthermore, slow Cu(II)-transport was observed, which necessitates the use of a larger membrane area.

The transport behaviour of several metal ions through PIMs and SLMs was investigated by Ulewicz and Radzyminska-Lenarcik [126]. The membrane phase contained the carrier 1-decyl-4-methylimida-zole dissolved in dichloromethane. The results showed that Zn(II) could be separated selectively from other ions, such as Cd(II), Co(II) and Ni(II), by both the PIM and SLM. However, the PIM showed higher selectivity coefficients and longer membrane stability (of up to 360 h), compared to the SLM configuration. On the other hand, a study by Baczyńska et al. [127] compared PIMs and SLMs for the selective extraction of Zn(II), Fe(II) and Fe(III) from aqueous chloride solutions. Three phosphonium-based ILs were used, namely Cyphos IL 101, 104 and 167. The results showed that the highest initial fluxes and permeability coefficient of Zn(II) was achieved for the SLM, containing Cyphos IL 167. On the one hand, PIMs showed a more efficient separation of Zn(II) and Fe(III) from Fe(II). On the other hand, SLMs were observed to be more stable in consecutive extraction and washing steps. Therefore, depending on the needs, it may be opted to use PIMs of SLMs, respectively.

The extraction of alkali metals by SLMs is also investigated in literature. Garifzyanov et al. [128] studied transport properties of Li(I), Na(I) and K(I) through a PTFE film, impregnated with a carrier in kerosene. The used carriers were N,N-bis(dihexyl-phosphoryl-methyl)-octylamine (**I**) and didecylthiophosphorus (**II**) or didecyldithiophosphorus (**III**) acids. If **I** and **II** are combined, a synergetic mixture is achieved, which showed the highest Li(I)-flux and an acceptable selectivity. Another study by Garipova et al. [129] investigated a similar case, in which Li(I) and Na(I) were selectively separated by a PTFE membrane, impregnated with another synergetic mixture. The membrane phase contained an acidic carrier 2-ethylhexyl hydrogen [bis(2-ethylhexyl)amino]-methyl-phosphonate and its neutral analog dihexyl(octylaminomethyl)phosphine oxide dissolved in kerosene. It was shown that a small synergetic effect occurred, causing an increased selectivity for Li(I)-ions. Zante et al. [130] investigated the use of ILs for the selective separation of Li(I) from aqueous solutions containing Na(I), Co(II) and Ni(II). The PVDF membrane was impregnated with the carrier TBP dissolved in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The Li(I)-ions were selectively extracted from the feed containing large amounts of Na(I)-ions. However, the membrane stability was closely related to the IL density and solubility in the surrounding phases. Its stability could be improved by addition of salt in the feed and/or stripping phase. Instead of using ILs for stability improvement, Song et al. [131] used a blended membrane, consisting of PES and SPPESK, for Li(I)-extraction. At a PES/SPPESK ratio of 6/4, the best performance was achieved, with a high Li(I)-flux. The membrane remained stable for 50 days, before a slight decline in elongation was noticed.

4.2.2 Rare earth element recovery

As mentioned before, rare earth elements are used for many electronic devices, such as cell phones, computers and rechargeable batteries. The recycling of post-consumer products to recover rare earth elements provides significant benefits,

regarding air emissions and ground-water contamination, when compared with rare earth elements mining processes. Kim et al. [125] and Kim et al. [132] discussed the use of a hollow fibre membrane contactor to recover neodymium (Nd), praseodymium (Pr) and dysprosium (Dy) from commercial and industrial magnets. A multi-membrane configuration showed a high selectivity for rare earth elements-extraction from aqueous nitric feed streams, without co-extraction of non-rare earth elements. The rare earth element oxides could then be recovered from the strip solution through precipitation and drying.

Next to the selective separation of rare earth elements from non-rare earth elements, different studies have been published for the extraction of specific rare earth elements. Pavon et al. [133] investigated the selective extraction of Nd(III) from Tb(III) and Dy(III), present in a chloride solution containing waste magnets. A flat sheet, SLM setup was used and the results suggested that Cyanex 572 was a better carrier for Nd(III)-separation, compared to Cyanex 272. Vernekar et al. [134], on the other hand, presented a mathematical model for Nd(III)-extraction from nitrate media by a hollow fibre module, impregnated with TODGA diluted in *n*-dodecane. The developed model was not specific to the studied case alone, thus enabling its more general and wider applicability.

Different studies were performed for rare earth elements-extraction of Dy(III) and Eu(III) in an SLM setup, using a flat sheet, PTFE membrane. Zaheri et al. [135] studied the pertraction of Dy(III), with D2EHPA in kerosene as the membrane phase. Optimal experimental conditions, leading to the highest extraction efficiency, were determined, regarding the feed pH and the feed and strippant concentration. The SLM stability was found to be satisfactory over a period of 6 days. The extraction of Eu(III) was investigated by Zaheri et al. [136] with Cyanex272 and D2EHPA in kerosene as the carrier solution. Again optimal extraction conditions were determined, whilst the membrane remained stable for over 9 days. A follow-up study by Zaheri et al. [137] discussed the use of multi-walled carbon nanotubes (MWC-

NTs) in the membrane phase to enhance the permeation of Eu(III). The presence of MWCNTs indeed increased the permeability coefficient of Eu(III), because they act as a solute sorbent. The membrane remained stable for 10 cycles of operation, but the use of CNTs lowered the SLM-stability, because of hydrophilic interactions. Zaheri et al. [138] also investigated the synergistic extraction of Dy(III) and Eu(III) with Cyanex 272 and D2EHPA in kerosene as the membrane phase. At a molar ratio of 0.4/0.6 for Cyanex 272 and D2EHPA, the maximum separation factor for Dy(III) from Eu(III) was achieved. The membrane remained stable for 6 cycles of operation, indicating its use in efficient liquid membrane systems for selective Dy(III)-pertraction.

The use of nano-liquids present in the membrane was investigated by Tehrani and Rahbar-Kelishami [139]. A PTFE SLM-setup was used for gadolinium (Gd) extraction, which was impregnated with a nano-liquid, consisting of hydrophilic TiO_2- or hydrophobic SiO_2-nanoparticles and Aliquat 336 in kerosene. The hydrophilic nanoparticles gave the highest permeability coefficient, possibly because they have a lesser tendency to reach the membrane interface. Stability tests showed a slight reduction of the permeation after 10 cycles of operation, but the SLM without nanoparticles had a lower reduction of the permeation coefficient. A follow-up study by Mohammad Tehrani and Rahbar-Kelishami [140] investigated the extraction of Gd(III) and Nd(III) from aqueous media, by using nano-liquids. An improvement of almost 30 and 50 % of the Gd(III)- and Nd(III)-permeability coefficient was observed, respectively. Furthermore, it was shown that an increase in the concentration and the size of the nanoparticles led to the aggregation of nanoparticles, resulting in pore blockage and decreased performance. Therefore, a maximum limit should be set for the nanoparticles' size and concentration.

Ionic liquids were also investigated as an alternative membrane phase for rare earth elements-extraction. Didi and Elhabiri [141] investigated the use of Cytos IL102 and D2EHPA for Tb(III)-extraction, by using a PVDF SLM-setup. A previ-

ous study by Elhabiri and Didi [142] also checked Tb(III)-transport, but without the use of ILs. An SLM-setup was built, using a PVDF membrane, impregnated with D2EHPA and TOPO, dissolved in diethyl ether. A process optimization was performed and the optimal yield was achieved after 4 hours and a stirring speed of 900 rpm for both studies. The amount of Tb(III) extracted was 4.37 and 8.29 mg per gram of extractant for an initial Tb(III)-concentration of 10^{-3} M with and without the use of an IL, respectively. Thus, the use of an ionic liquid decreased the extraction yield of Tb(III). However, a study by Asadollahzadeh et al. [143] investigated Ce(III)-transport through PTFE membranes, impregnated with the IL $[C_6MIM][NTf_2]$ (**I**) or $[C_6MIM[[PF_6]$ (**II**), TBP and D2EHPA. It was found that (**I**) had a better synergistic effect with TBP and D2EHPA, leading to a higher permeation coefficient of Ce(III). Furthermore, the membrane was stable during three cycles of operation and showed a higher stability than the membrane with only D2EHPA as the carrier. The use of ILs could thus decrease extraction efficiency, but improve membrane stability.

4.2.3 Wastewater treatment

Textile waste waters contain toxic compounds and dyes, which need to be removed before discharge into the environment. Methylene blue (MB) is a common compound for dyeing of wool, silk and wood. Many dye removal techniques exist, such as adsorption, nanofiltration and even removal by aerobic and anaerobic biological processes. The use of a PTFE SLM-setup for MB-removal was investigated by Kazemi et al. [144]. Sesame oil was used as an efficient and environmentally friendly membrane phase and a mixture of D2EHPA and M2EHPA were used as the carriers. An optimization of the process parameters was performed, resulting in a 62 % MB-removal efficiency after 7 hours of operation. This could be improved by increasing the membrane contact area per unit volume. The system remained stable for 28 hours, before a decreased permeability was observed. A study by Isanejad

et al. [145] used a similar setup, but investigated the use of amine modified ZIF-8 nanoparticles for the removal of methylene blue (MB) and Rhodamine B (RhB). The optimal pertraction efficiencies of MB and RhB after 10 hours were 88.3 and 99.1 %, respectively. These nanoparticles thus improved the removal significantly. Mahdavi et al. [146], on the other hand, investigated the use of different nanoparticles, including hydrophilic (ZnO and TiO_2) and hydrophobic (ZIF-8 and Fe_3O_4) particles. It was found that hydrophobic particles increase the pertraction efficiency, with ZIF-8 being the most efficient. However, the optimum pertraction efficiencies of MB and RhB were 79.4 and 90.6 %, which is lower than in the previous study by Isanejad et al. [145]. These studies still indicate that the use of nanoparticles increase the pertraction efficiency of textile dyes.

Next to contaminants in textile waters, some industrial processes generate large quantities of wastewater, containing metal ions. The metallurgical industry, for example, produces chromium-contaminated wastewater. Precipitation, ion exchange and extraction technology are the most common methods for chromium removal. Religa et al. [147] investigated the selective separation of Cr(III)- and Cr(VI)-ions. DNNSA (dinonylnaphthalene sulfonic acid) and D2EHPA were used as the membrane carriers. Because of high carrier deactivation under strong oxidation of Cr(VI)-ions, DNNSA cannot be used practically for Cr(III)-separation. D2EHPA, however, ensures a high efficiency and selectivity, but only from diluted Cr(III)/Cr(VI)-mixtures. By decreasing the Cr(VI)-concentration and increasing the stirrer speed, to prevent the formation of polarizing layers near the membrane, higher concentrations can be used. A study by Rajewski and Religa [148] investigated the selective removal of Cr(III) using another membrane phase, consisting of D2EHPA and Cyanex 272, dissolved in o-xylene and kerosene. They showed that the use of Cyanex 272 and D2EHPA, compared to the sole use of D2EHPA, increases the Cr(III)-transport flux through the membrane fourfold. Furthermore, the use of Cyanex 272 stabilizes the transport structure, leading to longer SLM lifetimes. More specifically,

the membrane with D2EHPA and Cyanex 272 showed no sign of decreased performance until the sixth cycle of operation, after which a decrease of 25 % was observed. A follow-up study by Rajewski et al. [149] confirmed the synergistic effect of the selected carriers and proposed a mathematical model to describe the transport process. The removal of Cr(VI)-ions was investigated in two other studies. Rodríguez de San Miguel et al. [150] investigated the use of a flat sheet SLM-setup, with Cyphos IL101 as the carrier for Cr(VI)-removal. Under optimal process conditions, a Cr(VI)-recovery of 90 % was reached after 5 hours of pertraction. A further study by Jahanmahin et al. [151] used a similar flat sheet SLM-setup, with Aliquat 336 and TBP dissolved in kerosene as the membrane phase. This led to an even higher Cr(VI)-removal rate of 94.63 %.

Cadmium and lead are other important contaminants, which are released by different industries, such as the pulp and paper, fertilizer en petrochemicals industries. Bhatluri et al. [152] investigated the use of a flat sheet, PVDF SLM-setup, using Aliquat 336 in coconut oil as the membrane phase. At optimal conditions, Cd(II) and Pb(II) were extracted with a recovery of 67 and 78 % during simultaneous transportation. Lead was transported preferentially through the SLM, due to its favourable electronic configuration. The use of coconut oil in the membrane led to an increased stability of at least 40 hours. In a follow-up study by Bhatluri et al. [153], a similar setup was used, but D2EHPA was used as the membrane carrier, whilst sodium carbonate was used as the stripping agent. This resulted in the precipitation of Pb(II) and Cd(II) carbonate salts in the stripping solution, positively affecting the solute transportation. Nickel is also a common wastewater contaminant, coming from several sources, such as the electroplating and battery manufacturing industries. Whilst leaching, precipitation and adsorption are traditional methods used for nickel extraction, Sulaiman et al. [154] proposed the use of a stable SLM-setup, containing a composite PVDF/SPEEK membrane with D2EHPA and 1-octanol dissolved in refined palm oil as the membrane phase. The results

indicated that about 100 % of nickel was recovered after 14 hours of operation. Furthermore, the SLM lifespan was extended up to nine cycles with lower membrane and extractant weight loss. For a review of SLM-applications on the removal of arsenic, the paper by Marino and Figol [23] can be consulted.

Pharmaceuticals are another important contaminant. An example is acetaminophen or paracetamol (Ac), which is an active ingredient used in many pharmaceutical products. Apart from solid phase extraction or membrane filtration techniques, the use of a flat sheet SLM-setup for Ac-removal was studied by Kouki et al. [155]. The IL Aliquat 336 dissolved in octan-2-ol was used as the membrane carrier. An Ac-recovery of approximately 70 % was obtained, under optimal experimental conditions, thus showing its promise for industrial extraction purposes. The removal of another pharmaceutical, namely the antibiotic amoxicillin, was studied by Pirom et al. [156] in a hollow fibre SLM-setup, containing Aliquat 336 dissolved in 1-decanol as the membrane phase. The resulting removal efficiency was 89.75 %, which showed that the use of a HFSLM enabled high removal of amoxicillin. Apart from pharmaceutical compounds, silver ions can also be present in pharmaceutical or medical wastewater. Wongsawa et al. [157] studied Ag(I)-removal by a hollow fibre SLM-setup with Cyanex 923, D2EHPA or LIX 84-I as the carrier dissolved in kerosene. The setup achieved a high Ag(I)-removal efficiency of 98 %, for the optimal process conditions. Xue et al. [158], on the other hand, discussed the removal of cyanides from aqueous solutions by a flat sheet, PVDF SLM-setup, impregnated with [Bmim]PF_6 in kerosene. The results showed that a removal efficiency of up to 95.31 % was reached. The studies by Wongsawa et al. [157] and Xue et al. [158] show the potential of ILs for removal of Ag(I) and cyanide from aqueous waste streams.

The use of pesticides necessitates the removal of these compounds, before discharge of industrial wastewater or run-off from agricultural land into water sources. Dordević et al. [159] tested a hollow fibre SLM-setup for the extraction of five different pesticides, namely acetamiprid, dimethoate, imidacloprid, linuron and

tebufenozide. TOPO dissolved in di-*n*-hexyl ether was used as the membrane phase. A maximum removal efficiency of 95 % was achieved for the most non-polar pesticide tebufenozide. The removal of the polar pesticides was significantly hindered by the presence of the organic phase in the pores. However, a large majority of each pesticide was removed from the feed and entrapped in the organic phase, which could be recovered by rinsing the membrane with methanol. A further study by Đorđević et al. [160] found that by using feed recirculation the maximum removal of polar pesticides could be increased from 30 to 86 %, when compared with the continuous single-pass operation.

Not only supported liquid membranes in a flat sheet or hollow fibre configuration are promising techniques for contaminant removal. The use of a hollow fibre renewal liquid membrane (HFRLM) was also investigated. Ren et al. [161] and Ren et al. [162] proposed the use of HFRLM, in which phase droplets are dispersed in the tube side of the hollow fibre. The droplets update the liquid film layer constantly, reducing the liquid membrane loss. Liu et al. [163] investigated the use of the HFRLM-technique for ammonia removal. The feed was pumped through the shell or the lumen side of the setup, whilst the strippant on the other side. The extractant phase, which consisted of D2EHPA dissolved in kerosene, was dispersed in the lumen phase. For an initial feed concentration of around 160 mg/L, the concentration was reduced to less than 15 mg/L after 4 hours of operation. These results then showed that the HFRLM technique was feasible for the treatment of ammonia wastewater.

4.2.4 Membrane extraction for the nuclear industry

Although conventional solvent extraction is a promising method for the treatment of nuclear fuels, due to its high efficiency, it has some inherent drawbacks, such as production of large amounts of organic waste. The use of membrane extraction reduces the required amount of organic solvent and limits extractant degradation and

emulsion formation. Furthermore, the use of SLMs can be used for the separation of elements in spent nuclear fuel. A PTFE SLM-setup, impregnated with HDEHP or TBP in *n*-dodecane, was used by Nee and Nilsson [164] for the extraction of Nd(III) or Ce(III), respectively. Nd(III)- and Ce(III)-extraction efficiencies of up to 80 and 75 % were achieved in the setup. The membrane remained stable for over 33 hours of contact with a 7 M nitric acid solution. The results of these experiments were then used to test the possibility of partitioning curium (Cm) from americium (Am) through a membrane, supported with TBP. However, the experimental transport rates of both Am(VI) and Cm(III) were very slow, when compared to the results of the Nd(III)- and Ce(III)-extraction. Possible causes for these reduced rates are the incomplete oxidation of Am(III) to Am(V) and Am(VI)-reduction on the membrane surface.

The major challenges at the end of a nuclear fuel cycle are the management of high level waste. More specifically, actinide partitioning is a key step for reduction of the radiotoxicity of nuclear wastes. This involves extraction of trivalent actinides and lanthanides from the high level waste, containing actinides, fission products elements and process chemicals in a nitric acid medium. Diglycolamide (DGA) extractants, such as TODGA (N,N,N′,N′-tetra-n-octyl diglycolamide) and T2EHDGA (N,N,N′,N′-tetra-2-ethylhexyl diglycolamide), have been studied extensively in actinide partitioning experiments. Panja et al. [165] investigated the transport behaviour of Eu(III) using five DGA extractants, namely TPDGA (N,N,N′,N′-tetra-*n*-pentyl diglycolamide), THDGA (N,N,N′,N′-tetra-*n*-hexyl diglycolamide), TODGA, T2EHDGA and TDDGA (N,N,N′,N′-tetra-*n*-decyl diglycolamide) by employing a PTFE-membrane. By using 30 % isodecanol as a phase modifier, third phase formation was hindered to a large extent. The study found that TDDGA and TPDGA were the most suitable extractants for Eu(III)-transport. However, TODGA may still be preferred, since TPDGA has a significant water solubility and TDDGA showed a limited performance if isodecanol is present. Another study by Sinharoy et al. [166]

tested the selective separation of Sr(II) and Eu(III), by using a flat sheet, PTFE membrane with TEHDGA (N,N,N′,N′-tetra(2-ethylhexyl) diglycolamide) as the membrane carrier. This process enabled the recovery of Sr(II), almost free of Eu(III)-contamination.

The use of benzene-centered tripodal diglycolamide (Bz-T-DGA) ligands for the extraction of Am(III) through flat sheet, PTFE membranes was investigated by Mahanty et al. [167]. Three different ligands, which were referred to as **L-I**, **L-II** and **L-III**, were used in this study. The Am(III)-transport was quantitative with ligand **L-I**. **L-III** showed a higher transport efficiency than **L-II**, but still lower than the rates of ligand **L-I**. The extraction efficiency for the actinide ions was Am(III) > Pu(IV) > UO_2^{2+}, suggesting its use for decontamination of uranium and the remediation of radioactive wastes. The membrane stability was poor for all ligands, except for **L-I**. A scale-up by using hollow fibre contactors is required to improve throughput. A follow-up study by Mahanty et al. [168] tested two other Bz-T-DGA ligands, namely TPAMTEB and TPAETEB, in a similar flat-sheet, polypropylene setup. The ligands were dissolved in an isodecanol/*n*-dodecane mixture. The Am(III)-extraction was more than 90 % with TPAMTEB, compared to only 28.3 % for TPAETEB. The extraction order was Pu(IV) > Am(III) > U(VI) for both ligands. The Am(III)/Pu(IV)-selectivity was better for TPAETEB. The permeability data in this study indicated that TPAMTEB was far more efficient than previously used tripodal DGA-ligands and DGA-TREN. However, the membrane stability was poor, due to carrier loss from the membranes.

Mahanty et al. [169] tested the use of three N-pivot T-DGA ligands, namely iPr_3-TREN-DGA, TREN-DGA and TRPN-DGA, which were dissolved in a mixture of *n*-dodecane and isodecanol. They used a PTFE membrane for the SLM-configuration. iPr_3-TREN-DGA had an isopropyl substituent and a C_2-spacer, whilst TREN-DGA and TRPN-DGA had a C_2- and C_3-spacer, respectively, without an isopropyl substituent. iPr_3-TREN-DGA showed the highest Am(III)-extraction efficiency, possi-

bly due to its higher lypophilicity, whilst the membrane stability was the highest if TRPN-DGA was used. However, the SLM-stability was not satisfactory, suggesting the need for intermittent carrier replenishment. A further study by Mahanty et al. [170] tested the use of iPr_3-TREN-DGA and TRPN-DGA for the pertraction of Np(IV) and Pu(IV) from aqueous nitric acid media, by a PTFE membrane. iPr_3-TREN-DGA showed the highest extraction for the tetravalent actinides. Again, the membranes showed poor stability, limiting their long term use.

A study by Mohapatra et al. [171] tested Am(III)-extraction through a PTFE membrane, supported with one of three different DGA-functionalized calix[4]arenes, which were referred to as **L-I** (lower-rim), **L-II** (upper-rim) and **L-III** (both-side). These carriers were compared with TODGA as the membrane carrier under identical conditions, which showed that **L-III** extracted tetravelant actinide ions (Pu(IV)) to a greater extent than trivalent ions (Am(III)), compared to TODGA. The transport efficiency of the carrier was Eu(III) > Pu(IV) > Am(III) > UO_2^{2+}. However, the SLM showed a very poor stability, nullifying the extraction efficiency. Mohapatra et al. [171] proposed to test PIMs containing the used ligands or grafted membranes for stability improvement. Another study by Ansari et al. [172], tested three DGA-functionalized dendrimers, namely **L-I** (2 DGA-moieties), **L-II** (4 DGA-moieties) and **L-III** (8 DGA-moieties), as membrane carriers in SLMs for the recovery of trivalent actinides over uranium. They were dissolved in a mixture of *n*-dodecane and *iso*-decanol. The SLM-setup consisted of a flat sheet, PTFE membrane, impregnated with the carrier solution. Carriers **L-II** and **L-III** showed quantitative transport of Pu(IV), Am(III) and Eu(III) in around 5 hours. In addition, the SLM showed an improved stability over a period of 5 days.

Apart from minor actinides, such as americium and curium, high level waste-streams also contain fission products, which pose a long-term radiation hazard, such as cesium. Various methods have been proposed for Cs(I)-separation, such as the use of chlorinated cobalt dicarbollide (CCD) as the extractant. Kandwal and

Mohapatra [173] proposed a flat sheet, PTFE SLM-configuration, impregnated with CCD dissolved in NPOE (2-nitrophenyloctyl ether) and *n*-dodecane. At optimized conditions, a metal extraction of 87.8 % was reached. Furthermore, the membrane showed sufficient stability for low to moderate feed acidity. A study by Raut et al. [174] tested the recovery of radio-cesium from high level waste-streams by two calix-crown ligands, namely CNC (calix[4]-bis-2,3-naptho-crown-6) and BOCMC (bis-(octyloxy)-calix-[4]-arene-mono-crown-6), in different diluents. By using BOCMC dissolved in an NPOE/*n*-dodecane-mixture, Cs(I)-extraction efficiency of up to 91.1 % was reached. In addition, the PTFE membrane remained stable over a period of 20 days. A further study by Jagasia et al. [175] tested a solution of four calix-crown-6 ligands, namely CC (calix[4]arene-biscrown-6), CBC (calix[4]arene-benzo-bis-crown-6), CNC (calix[4]arene-naphtho-bis-crown-6) and CMC (bis-(octyloxy)-calix-[4]-arene-mono-crown-6), dissolved in PTMS (phenyltrifluoromethyl sulfone) and Alamine 336, for the pertraction of radio-cesium. The extractants were immobilized in a PTFE membrane. CBC was found to be the most suitable candidate for Cs(I)-pertraction. Furthermore, the transport rates were found to be faster, compared to using these ligands in other diluents, such as nitrobenzene or an NPOE/*n*-dodecane mixture. A stability analysis indicated that appropriate performance for a few days, after which a sharp fall in Cs(I)-transport was observed. The use of a hollow fibre module may then be used to increase throughput.

Uranium is one of the most important metals used for the generation of nuclear power. It can be recovered from multiple sources, e.g., molybdenum production residue. Fourie et al. [176] dissolved this residue in nitric acid and tested uranium extraction by TBP through a polypropylene membrane. By using ammonium carbonate as the stripping phase, up to 99 % of U(VI)-extraction efficiency could be achieved. Another study by Kumar et al. [177] compared the use of TBP with a series of mono-amides, namely N,N-dihexylhexanamide (DHHA), N,N-dihexyloctanamide (DHOA) and N,N-dihexyl-decanamide (DHDA), as the carrier

ligands, which were impregnated in a PTFE membrane. The experiments showed that the mono-amides could be used as alternatives to TBP for U(VI)-extraction, reaching uranium transport of more than 90 %. The use of a hollow fibre module can be investigated, in which the membrane surface area can be tailored. Next to the SLM-configuration, Zahakifar et al. [178] published a study in which uranium extraction was performed using a hollow fibre renewal liquid membrane (HFRLM). In this technique, the acceptor flows through the shell, whilst a mixture of the organic and donor phase flows through the porous hollow fibres. The dispersed organic drops then stick to the inner fibre walls to prevent LM loss. Compared to the HFSLM, the HFRLM-setup showed a five times longer stability, presenting its potential for industrial uranium extraction. A follow-up study by Yadollahi et al. [179] investigated the use of a polypropylene HFRLM for the selective extraction of a Zr/Hf-mixture. The HFRLM showed a mass transfer coefficient which was two times higher compared to the HFSLM-setup and was stable for up to 700 minutes of continuous operation.

The PUREX process is used to reprocess irradiated nuclear fuels. More specifically, uranium and plutonium are separated from fission products. TBP dissolved in *n*-dodecane co-extracts both uranium and plutonium, which leaves a majority of the fission products in the waste stream. Plutonium is then partitioned from uranium by using a suitable carrier agent. Singh et al. [180] tested selective Pu(IV)-extraction from other impurities, using Aliquat 336 in *n*-paraffin as the carrier, immobilized in a PTFE membrane. More than 80 % of plutonium transport was achieved at a 10 % w/v concentration of Aliquat 336. The optimized system could be used for plutonium purification processes. In a study by Sivaramkrishna et al. [181], two diamide ligands with a tri-aryl-pyridine (TAP) bridge, namely N,N-di-n-octyl-TAP-diamide **L-I** and N,N-dioctyl-PDAP-diamide **L-II**, were tested as selective carriers for Pu(IV)-extraction through a PTFE membrane. An extraction efficiency of 90 % was reached

with **L-I** in about 5 hours with an excellent Pu(IV)-selectivity. The membrane remained stable over a period of 10 days, indicating its excellent performance.

The separation of thorium is another extraction process, utilized for the treatment of nuclear waste. Dinkar et al. [182] studied Th(IV)-extraction by using a flat sheet, PTFE membrane, impregnated with Cyanex 923 as a carrier. After process optimization, a Th(IV)-extraction efficiency of more than 90 % was achieved. However, the membrane is subject to stability improvement. Allahyari et al. [183] investigated the use of a polypropylene HFRLM with Cyanex 272 diluted in kerosene as the carrier. The feed/carrier mixture was pumped through the lumen side, whilst the receiving solution was pumped through the shell side of the module. The HFRLM-module presented an extraction efficiency up to 100 % and remained stable for 10 hours of continuous operation, showing its industrial potential. Lastly, high level waste-solutions contain high levels of palladium, which could be used in various fields, such as the electric and pharmaceuticals industry. Panja et al. [184] studied the use of a novel ligand, namely DTDGA (N,N,N′,N′-tetra-(2-ethylhexyl)-dithiodiglycolamide), for the selective extraction of Pd(II) from nitric acid media through a PTFE membrane. Almost quantitative palladium transport with a high selectivity was achieved in a 2 hour interval. Membrane stability was sufficient for 6 cycles of operation. Another application is the selective separation of yttrium, which is used for radionuclide therapy, from strontium. Petrović et al. [185] tested the use of a hollow fibre SLM with D2EHPA in dodecane as the membrane phase. A Y(III)-yield of up to 72 % was achieved with a co-extraction of Sr(II) of 0.2 %. This system could then be used for the development of an yttrium generator, coupled with direct complexation for the preparation of radiopharmaceuticals.

4.2.5 Other extraction applications

Petroleum industries are expected to reduce sulphur emissions and use desulfurization technology to comply with governmental regulations. Apart from the tra-

ditional treatment, namely catalytic hydrodesulfurization, liquid-liquid extraction is an attractive alternative. Ferreira et al. [186] focused on the use of ILs as alternative solvents for thiol removal from *n*-dodecane as a model stream for jet fuels. Three 1-ethyl-3-methylimidazilium cation-based ILs were used, which increased mass transfer resistance, due to their inherent high viscosity. The SILMs demonstrated a good stability, but the permeation of *n*-dodecane was undesirably high. This problem was solved by employing a hollow fibre module, in which the IL $[C_2mim][CF_3SO_3]$, which has a low *n*-dodecane solubility, flowed countercurrently with the feed. However, two membrane contactors are then needed for the extraction and stripping step.

Membrane extraction using SLMs can also be applied in the biochemical or food sector. The downstream processing of amino acids, which are important bioactive substances, is conventionally performed by centrifugation or membrane filtration for cell removal. Mahdavi et al. [187] used a flat sheet, PTFE SLM, impregnated with a mixture of M2EHPA and D2EHPA in kerosene, for L-lysine removal. After process optimization, an extraction efficiency was observed of only 33.4 %. The stability of the process was related to the pertraction efficiency, which decreased by less than 7 % after 8 hours. However, changing the configuration to an ELM or BLM increases the separation performance to 100 and 97 %, respectively. Another application, namely the extraction of citric acid, was studied by Chanukya et al. [188] in an SLM with Aliquat 336 in toluene as the membrane phase. Almost complete citric acid extraction was achieved, when sodium salts were used as the strip solution. This technique could be used for the removal of citric acid from lemon, orange and sweet-lime juices.

Lastly, SLM-configurations were studied, with respect to the organics and inorganic acids industry. Two studies, by Blahušiak et al. [189] and Kamal et al. [190] showed the potential of SLMs during the production of butyric and phosphoric acid, respectively. More specifically, SLMs could be used for extractive fermentation of

butyric acid or for the removal of vanadium ions, a common impurity in phosphoric acid preparation. The SLM-technology could also be interesting for the biomedical sector. Urea is mainly removed from blood by haemodialysis membranes, but the selectivity of these membranes is dependent on the molecular weight of the transported species and not by specific interactions. The use of SLMs for urea removal is investigated by Joshi et al. [191]. Three types of membranes (PTFE, dialysis and eggshell membranes) were impregnated with a receptor solution, containing a receptor dissolved in chloroform. Six receptors were tested and the results show that receptors, containing acetoacetate ester groups, show a higher urea complexation than simple glycol receptors, making them more suitable carriers for urea extraction.

Table 14: Supported liquid membrane-based extraction processes used for different industries. The number in the first column indicates the industrial branch: organics industry (1), metallurgical and mining industry (2), wastewater treatment (3), high level waste treatment (4), rare earth elements extraction (5), petrochemical and fuel industry (6), medical and biomedical industry (7), biochemical and food industry (8), phosphoric acid industry (9).

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
2	Aqueous HCl-solution with Fe(III), Zn(II), Cd(II) and Cu(II)	$[MTOA^+][Cl^-]$	Milli-Q water, Na_2CO_3 (0.1 M) or NH_3 (6 M)	Flat sheet, hydrophilic polyamide membrane; pertraction factors (defined as the ratio of stripping and feed concentration) of 9, 373 and 15.1 were reached for Fe(III), Zn(II) and Cd(II) by using the following stripping phases, milli-Q water, Na_2CO_3 (0.1 M) or NH_3 (6 M); the membrane showed remarkable stability up to 456 hours	[120]
2	Aqueous solution of Cd(II) and Zn(II)	D2EHPA, M2EHPA, Cyanex-302 or TBP in kerosene	Aqueous H_2SO_4-solution	Flat sheet, microporous PTFE membrane; a maximum Cd(II)- and Zn(II)-permeability of 4.42 10^{-5} and 3.63 10^{-5} mols m/s was reached after 6 hours for M2EHPA; D2EHPA and Cyanex 302 showed lower permeabilities	[121]
2	Aqueous solution of Cd(II) and Ni(II)	D2EHPA and MEHPA in kerosene	Aqueous H_2SO_4-solution	Microporous, hydrophobic PTFE film; Cd(II)- and Ni(II)-recoveries of 83.3 and 0.45 % were reached after 24 hours, under optimal experimental conditions; the membrane stability decreased significantly after 36 hours	[122]

Table 15: Table 14 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
2	Aqueous ammonia/ammonium chloride solution of Ni(II)	Acorga M5640 in kerosene	Aqueous H_2SO_4-solution	Flat sheet, PVDF membrane; almost quantitative Ni(II)-transport was achieved after 18 hours of operation under optimal conditions; the permeability coefficient was 9.28 10^{-6} m/s; the use of higher temperatures and ultrasonic assistance improved Ni(II)-transport; the membrane remained stable for 7 cycles of operation	[123]
2	Aqueous solution of Cu(II)	Aliquat 336/Cyanex 272 in kerosene	Aqueous ammonia solution	Flat sheet, microporous PVDF membrane; Cu(II)-extraction efficiencies up to 95 % were reached; membrane fouling occurred after 4 hours of testing	[124]
2	Aqueous solution of Zn(II), Cd(II), Co(II) and Ni(II)	1-decyl-4-methilimidazole in dichloromethane	Double distilled water	Flat sheet, microporous polypropylene membrane; the Zn(II)-recovery was above 95 % for both the PIM- and SLM-configuration; the PIM remained stable for 120 hours	[126]

Table 16: Table 15 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
2	Aqueous HCl-solution of Zn(II), Fe(II) and Fe(III)	Cyphos IL 101, 104 and 167 in decanol/kerosene	Aqueous H_2SO_4-solution	Flat sheet, PVDF membrane; Zn(II)-, Fe(II)- and Fe(III)-extraction efficiencies of 80, 40 and 80 % were achieved; the SLM and PIM have a similar performance for Cyphos IL 101 and 167 as the metal carrier; the SLM showed a better stability for many cycles, compared to the PIM	[127]
2	Aqueous solution of Li(I), Na(I) and K(I)	Synergetic carrier mixture in kerosene	Aqueous H_2SO_4-solution	PTFE film; a Li(I)-Na(I)-selectivity between 18 and 28 could be achieved by using a **I** + **III** carrier mix and a pH of 8	[128]
2	Aqueous solution of Li(I) and Na(I)	Carriers in kerosene	Aqueous tartaric acid solution	Flat sheet, PTFE membrane; Li(I)/Na(I)-selectivity increases with tartaric acid concentration and increases slightly, when a mixture of carriers **1** and **2** was used; an optimal Li(I)- and Na(I)-permeability of 9.78 and 0.99 10^{-3} mol/(m^2min) was reached for the carrier mixture	[129]

Table 17: Table 16 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
2	Aqueous solution of Li, Na, Co and Ni	[C4mim][NTf2] in TBP	Aqueous Na_2CO_2-solution	Flat sheet, microporous PVDF membrane; a maximum Li(I)-permeability coefficient of 1.2 10^{-6} was reached, when it is present individually in the feed; the addition of other salts in the feed decreased the Li(I)-permeability down to 8.7 10^{-7}; membrane stability remained for two days	[130]
2	Aqueous LiCl-, $FeCl_3$- and $MgCl_2$-solution	50/50-mixture of TBP and kero-sene	Aqueous HCl-solution	Flat sheet, blend SPPESK/PES; a Li(I)-flux of 1.67 10^{-8} mol/(cm^2s) was reached at a PES/SPPESK ratio of 6/4 and a polymer concentration of 30 wt%; the membrane remained solvent-resistant for up to 50 days, but further ME-tests are needed to confirm the performance	[131]
5	Aqueous HNO_3-solution of NdFeB permanent magnets	TODGA, Cyanex 923, TBP and isoparaffin	Aqueous HNO_3-solution	Hollow fibre, polypropylene membrane; up to full Dy- and Nd-depletion was achieved by using TODGA and Cyanex 923; TODGA showed superior selectivity compared to Cyanex 923 for rare earth element separation from non-rare earth elements	[125, 132]

Table 18: Table 17 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
5	Aqueous solution of Nd(III), Tb(III) and Dy(III)	Cyanex 272 and Cyanex 572 in kerosene	Aqueous HCl-solution	Flat sheet, microporous PTFE membrane; Tb(III)-, Dy(III)- and Nd(III)-extraction efficiencies of 90, 90 and 15 % were reached for carrier Cyanex 572 at 0.75 M, leading to selective Nd(III)-separation; membrane stability remained acceptable for at least 24 hours	[133]
5	Aqueous HNO_3-solution of Nd(III)	TODGA and DHOA dissolved in *n*-dodecane	Distilled water	Hollow fibre, polypropylene membrane; up to full depletion of Nd(III) in the feed could be achieved using appropriate conditions for process parameters; simulated Nd(III)-extraction results were in good agreement with the experimental	[134]
5	Aqueous solution of Dy	D2EHPA in kerosene	Aqueous HNO_3-solution	Flat sheet, PTFE membrane; a Dy-permeability coefficient of 1.63 10^{-5} m/s was reached under optimal experimental conditions; the membrane remained stable over 6 cycles of operation	[135]

Table 19: Table 18 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
5	Aqueous HNO_3-solution of Eu	D2EHPA and Cyanex272 in kerosene	Aqueous HNO_3-solution	Flat sheet, hydrophobic, microporous PTFE membrane; a Eu-permeability coefficient of 3.48 10^{-5} m/s was reached under optimal experimental conditions; quantitative Eu-transport was achieved in 360 min; the membrane remained stable for 9 days; addition of multi-walled carbon nanotubes reduces the permeability coefficient and membrane stability	[136, 137]
5	Aqueous solution of Dy(III) and Eu(III)	D2EHPA and Cyanex272 in kerosene	Aqueous HNO_3-solution	Flat sheet, hydrophobic, microporous PTFE membrane; a mass transfer coefficient of 1.86 10^{-5} m/s was reached; the membrane remained stable for 6 cycles of operation	[138]
5	Aqueous $Gd(NO_3)_3$-solution	Aliquat-336 with SiO_2- and TiO_2-nanoparticles in kerosene	Aqueous HNO_3-solution	Flat sheet, microporous PTFE membrane; a maximal permeability coefficient of 12.57 10^{-5} m/s was reached for SiO_2-nanoparticles, which was 28.2 % higher than for the TiO_2-nanoparticles; the membrane remained stable for 10 cycles of operation	[139]

Table 20: Table 19 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
5	Aqueous solution of Gd and Nd	TiO_2- and SiO_2-nanoparticles and Aliquat-336 in kerosene	Aqueous HNO_3-solution	Flat sheet, microporous PTFE membrane; the dispersion of hydrophobic SiO_2-nanoparticles improved the Gd- and Nd-permeability by 28.3 and 49.5 %, respectively	[140]
5	Aqueous solution of Tb(III)	D2EHPA and Cytos IL102 in diethyl ether	N/A	Flat sheet, microporous PVDF membrane; an optimal yield of 100 % could be achieved after 120 minutes for an initial Tb(III)-concentration of 10^{-4} M; the yield decreased for lower stirring speeds and feed pH and higher feed concentration	[141]
5	Aqueous HNO_3-solution of Tb(III)	D2EHPA and TOPO in diethyl ether	Aqueous HNO_3-solution	Flat sheet, PVDF membrane; a maximum extraction yield of up to 90 % was reached under optimal experimental conditions	[142]
5	Aqueous solution of Ce(III)	[C6mim][NTf2] and [C6mim][PF6] in D2EHPA and TBP	Aqueous solution of H_2SO_4, HNO_3 or HCl	Flat sheet, microporous PTFE membranes; up to 79.73 % of Ce(III)-transport was achieved for a carrier mixture of [C6mim][NTf2] dissolved in D2EHPA and TBP; the permeability coefficient reached a maximum value of 9.22 10^{-5} m/s; the membrane was stable during three cycles of operation	[143]

Table 21: Table 20 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
3	Aqueous solution of methylene blue	Sesame oil with a mixture of D2EHPA and M2EHPA	Acetic acid	Flat sheet, PTFE membrane; an MB mass transfer coefficient of 5.63 10^{-6} m/s and an MB recovery of almost 62 % was reached at optimized values of initial feed, carrier and strippant concentration and feed pH; the membrane remained stable for four cycles of operation	[144]
3	Aqueous solution of RhB and MB dyes	M2EHPA, D2EHPA and nanoparticles in sesame oil	Aqueous acetic acid solution	Flat sheet, microporous PTFE membrane; loading of hydrophilic or -phobic nanoparticles decrease and increase extraction efficiency, respectively; optimal MB- and RhB-pertraction efficiencies of 88.3 and 99.1 % were reached after 10 hours of operation	[145, 146]
3	Aqueous solution of Cr(III) and Cr(VI)	DNNSA or D2EHPA in kerosene and o-xylene	Aqueous H_2SO_4-solution	Flat sheet, microporous PTFE membrane; a Cr(III)-flux of up to 4.6 10^{-5} mol/(m^2s) could be reached for D2EHPA; extraction time and initial Cr(VI)-concentration negatively affected the separation	[147]

Table 22: Table 21 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
3	Aqueous solution of Cr(III)	D2EHPA and Cyanex 272 in o-xylene and kerosene	Aqueous HCl-solution	Flat sheet, PTFE membrane; a maximum Cr(III)-flux (16.0 10^{-5} mol/(m^2s)) was reached, when a synergetic two-carrier mixture was used, compared to around 5.0 10^{-5} mol/(m^2s) for the use of the single carrier D2EHPA; the membrane remained stable for 5 cycles of operation	[148, 149]
3	Aqueous HCl-solution of Cr(VI)	CYPHOS IL101 in toluene	Aqueous NaOH-solution	Flat sheet, microporous PVDF membrane; a Cr(VI)-recovery of 90 % was reached from a 7 mg/L feed solution in 10 mM HCl medium after 5 hours of pertraction	[150]
3	Aqueous solution of Cr(VI)	Aliquat 336 and TBP in kerosene	Aqueous NaOH-solution	Flat sheet, PTFE membrane; a Cr(VI)-extraction rate of 94.63 % was achieved under optimal experimental conditions	[151]
3	Aqueous HCl-solution with Cd(II) and/or Pb(II)	Aliquat 336 in coconut oil	EDTA	Flat sheet, PVDF membrane supported with the solvent; Cd(II)- and Pb(II)-extraction efficiencies were 79 and 84 %; in a mixture, Cd(II)- and Pb(II)-recoveries were 67 and 78 %	[152]

Table 23: Table 22 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
3	Aqueous HCl-solution with Cd(II) and/or Pb(II)	D2EHPA in coconut oil	Aqueous Na_2CO_3-solution	Flat sheet, PVDF membrane; individual Cd(II)- and Pb(II)-extraction efficiencies of 82.48 and 92.53 % were reached; the lowest combined flux was reached at a 1:1 Cd(II):Pb(II)-ratio; the membrane remained stable for up to 100 hours	[153]
3	Nickel electroplating wastewater	D2EHPA and 1-octanol in refined palm oil	Aqueous H_2SO_4-solution	Flat sheet, composite SPEEK/PVDF membrane; up to full Ni(II)-depletion was achieved when 100 % refined palm oil was used; the SLM-lifespan was extended to 9 cycles of operation	[154]
3	Aqueous solution with acetaminophen (Ac)	Aliquat 336 in octan-2-ol	Aqueous NaOH-solution	Flat sheet, polypropylene and PVDF membrane; Ac-recovery of approximately 70 % was achieved under optimal experimental conditions; 60 % of Ac could be recovered from three other drugs in aqueous samples	[155]
3	Aqueous solution of amoxicillin	Aliquat 336, Alamine 336 and D2EHPA in various diluents	Aqueous NaCl-solution	Hollow fibre, polypropylene membrane; a maximum permeation coefficient of 2.778 10^{-4} m/s was reached after 60 minutes	[156]

Table 24: Table 23 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
3	Aqueous solution of Ag(I) and Fe(II)	Cyanex 923, D2EHPA and LIX 84-I in kerosene	Aqueous solution of thiourea and $Na_2S_2O_3 \cdot 5\ H_2O$	Hollow fibre, polypropylene membrane; a Ag(I)-removal efficiency of up to 98 % was reached under optimal experimental conditions	[157]
3	Cyanide-containing wastewater	[Bmim]PF_6 in kerosene	Aqueous NaOH-solution	Flat sheet, PVDF membrane; a cyanide removal of 95.31 % was reached under optimal experimental conditions	[158]
3	Aqueous solution with pesticides	5 v% TOPO in DHE	Aqueous HCl-solution	Hollow fibre, polypropylene membrane; a removal efficiency of 95 % was reached for the most apolar pesticide tebufenozide; recoveries for the other pesticides ranged from 26 to 76 %; employing feed stream recirculation significantly improves the efficiency from 30 to 86 %	[159, 160]
3	Wastewater with ammonia	D2EHPA in kerosene	Aqueous HCl-solution	Hollow fibre, polypropylene membrane; a removal efficiency of over 90 % was reached after 10 stages of the hollow fibre renewal liquid membrane cascade; better results were obtained when the feed flows through the shell side	[163]

Table 25: Table 24 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution of Am(III), Ce(III), Ce(IV), Cm(III), Nd(III)	HDEHP or TBP in *n*-dodecane	Aqueous HNO_3-solution	Flat sheet, PTFE membrane; Nd(III)- and Ce(IV)-extraction efficiencies of around 50 % were reached by using HDEHP or TBP as the carrier, respectively; combined Am(III)- and Cm(III)-extraction in TBP gave a low efficiency of only 10 %; stability of 33 hours was obtained	[164]
4	Aqueous HNO_3-solution with Eu(III)	0.1 M extractant solution (70% DGA and 30% isodecanol) dissolved in *n*-dodecane	Aqueous HNO_3-solution	Flat-sheet, microporous PTFE membrane; maximum Eu(III)-transport of 84.6, 73.5 and 92.9 % were achieved for TPDGA, TODGA and TDDGA; TODGA may still be preferred, because of its lower water solubility and performance in presence of the phase modifier	[165]
4	Aqueous HNO_3-solution of Eu(III) and Sr(II)	TEHDGA in isodecanol/n-dodecane	Aqueous HNO_3-solution	Flat sheet, microporous PTFE membrane; complete Eu(III)-transport was reached after 60 minutes, whilst only 10 % of Sr(II) was extracted, leading to a pure Sr(II)-stream	[166]

Table 26: Table 25 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution of Am(III), Pu(IV) and U(VI)	Bz-T-DGA ligands (TPAMTEB, TPAETEB) in isodecanol/n-dodecane	Aqueous HNO_3-, EDTA- or α-HIBA-solution	Flat sheet, microporous polypropylene or PTFE membrane; Am(III)-transport was as high as 90 % and as low as 28.3 % for TPAMTEB and TPAETEB, respectively; the membrane showed poor stability	[167]
4	Aqueous HNO_3-solution of Am(III), Pu(IV) and U(VI)	Bz-T-DGA ligands (**L-I**, **L-II**, **L-III**) in isodecanol/n-dodecane	Aqueous HNO_3-, EDTA- or α-HIBA-solution	Flat sheet, microporous polypropylene or PTFE membrane; Am(III)-, U(VI)- and Pu(IV)-extraction efficiencies of 87.7, 18.4 and less than 2 % were achieved for ligand **L-I**; transport rates were lower for the other ligands; the membrane was reasonably stable with **L-I**, whilst it was poor for **L-II** and **L-III**	[168]
4	Aqueous HNO_3-solution of Am(III)	Bz-T-DGA ligands (TREN-DGA, TRPN-DGA, iPr_3-TREN-DGA) in isodecanol/n-dodecane	Aqueous HNO_3-, EDTA- or α-HIBA-solution	Flat sheet, microporous polypropylene or PTFE membrane; up to 99.6 % of Am(III)-transport could be achieved by using iPr_3-TREN-DGA as the carrier and an aqueous solution of 0.1 M HNO_3 and 5.9 M $NaNO_3$ as the feed; the membrane showed poor stability	[169]

Table 27: Table 26 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution of Np(IV) or Pu(IV)	Bz-T-DGA ligands (TRPN-DGA, iPr_3-TREN-DGA) in isodecanol/n-dodecane	Aqueous HNO_3-, EDTA- or α-HIBA-solution	Flat sheet, microporous polypropylene or PTFE membrane; after 5 hours, iPr_3-TREN-DGA and TRPN-DGA showed the highest Np(IV)- and Pu(IV)-transport of 94.3 and 92.8 % in a feeds of different acidity; the membranes were not appropriately stable	[170]
4	Aqueous HNO_3-solution with Am(III), Pu(IV), Eu(III), U(VI), Cs(I) and Sr(II)	Diglycolamide-functionalized calix-[4]-arenes	Aqueous EDTA-solution	Flat sheet, PTFE membrane; Am(III)-, Eu(III)- and Pu(IV)-recoveries of 86.5, 99.9 and 99.9 % were achieved for a both-sided DGA-functionalized calix[4]arene as the carrier dissolved in pure *n*-dodecane; membrane showed very poor stability	[171]
4	Aqueous HNO_3-solution with high level waste-products (trivalent actinides and uranium)	DGA-carriers in iso-decanol/*n*-dodecane	Aqueous HNO_3-solution	Flat sheet, PTFE membrane; SLM with DGA-carriers **L-I**, **L-II** and **L-III** give Am(III)-extraction efficiencies of 0.76, 81.5 and 97.3 %, compared to 99.9 % for TODGA; the use of carrier **L-III** enabled nearly quantitative transport of Am(III), Eu(III) and Pu(IV) after 5 hours; the membrane remained reasonably stable over a period of 5 days	[172]

Table 28: Table 27 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution of Cs(I)	CCD in NPOE and *n*-dodecane	Aqueous HNO_3-solution	Flat sheet, PTFE membrane; metal ion extraction of 87.8 % could be achieved for an optimized solvent system of 1.0 10^{-2} M CCD in NPOE and *n*-dodecane; sufficient stability was obtained	[173]
4	HNO_3-solution with Cs(I)	BOCMC or CNC in 80% NPOE and 20% *n*-dodecane (0.4% Alamine-336)	Distilled water	Flat sheet, PTFE membrane supported with the solvent; Cs(I)-permeabilities of 2.23 10^{-4} and 3.26 10^{-4} cm/s were reached for CNC and BOCMC; up to 91.1 % of Cs(I) was transported after 24 hours; LM-stability remained for 20 days	[174]
4	Aqueous HNO_3-solution of Cs(I)	CC, CBC, CNC and CMC in PTMS and Alamine 336	Distilled water	Flat sheet, PTFE membrane; up to full Cs(I)-depletion could be achieved in aqueous Cs(I)-solutions; Cs(I)-extraction efficiency dropped to around 60 % in simulated mixed feeds; LM-stability remained for a few days	[175]
4	Aqueous $UO_2(NO_3)_2$-solution	TBP and kerosene	Aqueous $(NH_4)_2CO_3$ solution	Hollow fibre, polypropylene membrane; complete U(VI)-extraction was achieved at low feed concentrations; almost complete U(VI) stripping of 99 % was reached after a single contacting step	[176]

Table 29: Table 28 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution of U(VI)	DHHA, DHOA, DHDA or TBP in *n*-dodecane	Distilled water	Flat sheet, microporous PVDF membrane; up to 92 % of U(VI)-transport was reached after 4 hours for DHHA, suggesting the alternative use of these ligands to TBP; a decrease in the feed U(VI)-concentration decreased the extraction efficiency	[177]
2	Aqueous H_2SO_4-solution of U(VI)	Alamine-336 in kerosene	Aqueous NaCl-, NH_4Cl- or $NaHCO_3$-solution	Hollow fibre, polypropylene membrane; a maximum uranium recovery of 63.17 % was reached under optimal experimental conditions; the hollow fibre renewal liquid membrane remained stable for 12 hours, compared to only 2 hours for the SLM-setup	[178]
2	Aqueous HNO_3-solution of Hf and Zr	Cyanex-272 and TBP in kerosene	Aqueous NH_4F-solution	Hollow-fibre, polypropylene membrane; by using a hollow fibre renewal liquid membrane, the Zr-flux was increased from 90 to 190 10^{-7} mol/(m^2s), compared to the SLM-configuration; the Hf-flux remained low at values between 0 and 6 10^{-9} mol/(m^2s); good stability was kept for 700 minutes	[179]

Table 30: Table 29 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution of Pu(IV)	Aliquat 336 and *n*-paraffin	Aqueous HNO_3-solution	Flat sheet, microporous PTFE membrane; Pu(IV)-transport of more than 80 % was achieved at a feed acidity of 7.2 M and 10 wt% Aliquat 336 in *n*-dodecane	[180]
4	Aqueous solution of Am, Cs, Eu, Pu, Sr and U	*N,N*-di-n-octyl-TAP-diamide (**L-I**) and *N,N*-dioctyl-PDAP-diamide (**L-II**) in isodecanol/n-dodecane	Aqueous solution of NH_2OH and HNO_3	Flat sheet, microporous PTFE membrane; Pu(IV)-transport of up to 91.5 % was reached after 5 hours for **L-1**; the membrane showed poor stability in 10 days	[181]
2	Aqueous HCl-solution with Th(IV)	Cyanex 923	Aqueous ammonium carbonate solution	Flat sheet, hydrophobic, microporous PTFE membrane; thorium transport increased from 78.3 to 93.7 % by optimizing feed acidity, feed and membrane characteristics; carrier concentration; the membrane was relatively unstable, having a strongy reduced thorium transport (to 50 %) after already one cycle of operation	[182]
4	Aqueous nitrate solution of Th(IV)	Cyanex 272 in kerosene	Aqueous H_2SO_4-solution	Hollow fibre, polypropylene membrane; full Th(IV)-depletion was reached under optimal conditions; the OMTC was in the range of 5.7 10^{-8} to 2.41 10^{-7} m/s; the membrane was stable for 10 h	[183]

Table 31: Table 30 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
4	Aqueous HNO_3-solution with Pd(II)	DTDGA in *n*-dodecane	Aqueous HNO_3-solution with thiourea	Flat sheet, microporous PTFE membrane; up to full depletion of Pd(II) could be achieved at optimal experimental conditions (feed pH, carrier concentration, porosity, etc.); the membrane remained stable for six cycles of operation	[184]
6	Thiols in *n*-dodecane	[C2mim][$MeSO_4$], [C2mim][CF_3SO_3], [C2mim][NTf2]	N/A	Flat sheet, PVDF and PES membrane; low mass transfer coefficients between 0.67 and 2.01 10^{-7} m/s were achieved; this could be improved by using the ionic liquid as the receiving phase	[186]
7	Aqueous urea solution	Carriers in chloroform	Double distilled water	Egg-shell, PTFE and dialysis membrane; extraction efficiencies up to 50 % were reached by using carrier $\mathbf{R}_6$ in an eggshell membrane	[191]
7	Aqueous HCl-solution of Sr(II) and Y(III)	D2EHPA in dodecane	Aqueous HCl-solution	Hollow fibre, polypropylene membrane; a Y(III)-yield of 72 % was reached at an acceptor flow rate of 1.9 cm^3/min with a Sr(II)-breakthrough of 0.2 %	[185]

Table 32: Table 31 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
8	Aqueous solution of L-lysine monohydrate	M2EHPA and D2EHPA in kerosene	Aqueous HCl-solution	Flat sheet, microporous PTFE membrane; an L-lysine-pertraction efficiency of 33.4 % was reached under optimal experimental conditions; the membrane remained stable for 8 hours with a reduction in efficiency of 6.8 %	[187]
8	Citric acid in aqueous solutions and fruit juices	Aliquat 336 in toluene	Aqueous Na_2CO_3 and $NaHCO_3$-solution	Flat sheet, PTFE membrane; 100 or 33 % citric acid extraction was reached from different fruit juices after around 5 hours of operation, by using a $Na_2CO_3/NaHCO_3$-solution or de-ionized water as stripping solution	[188]
1	Aqueous solution with butyric acid	Oleyl alcohol in dodecane	Aqueous NaOH-solution	Flat sheet, PTFE membrane; a maximum mass transfer coefficient K_p of 2.3 10^{-4} m^2/s was reached for a pure dodecane solvent if the BA-concentration was higher than 0.45 $kmol/m^3$; for lower BA-concentrations, a maximum K_p was achieved, if oleyl alcohol was added to dodecane	[189]

Table 33: Table 32 continued.

No.	Source phase	Membrane phase	Receiving phase	Configuration, used membranes and results	Ref.
9	Aqueous HNO_3-solution of VO_2^+	Methyl cholate, resorcinarene or TOA in toluene	Aqueous HCl-solution	Flat sheet, microporous PVDF membrane; determination of the extraction mechanism and performance, based on nature and structure of the association site of each extractant; a maximum VO_2^+-permeability of 27.38 10^{-7} cm^2/s was reached for TOA	[190]
2	Aqueous HCl-solution of Au(III)	Cyphos IL101 in Solvesso 100	Water	Flat sheet, microporous PVDF membrane; an overall mass transfer coefficient of 3.2 10^{-5} m/s was achieved under optimal conditions	[192]
2	Aqueous HCl-solution of Au(III)	Different extractants in Solvesso 100	Water	Flat sheet, microporous PVDF membrane; Cyanex 923 and Cyphos IL 102 give the highest permeability coefficients of 4.9 and 4.1 10^{-5} m/s	[193]

4.3 Comparison and discussion of MBSE and SLM

As is clear from the previous sections, little to no industrial applications have been reported for both MBSE- and SLM-configurations. Mans et al. [74] proposed a methodology for the design of an industrial MBSE-column for Co(II)- and Ni(II)-recovery. Additionally, Kong et al. [109] reported an industrial MBSE-design for the removal of *p*-toluic acid from wastewater. The lack of industrial applications could be attributed to the lack of MBSE- and SLM-performance, related to selectivity and stability. Therefore, the current literature on MBSE- and SLM-applications focussed on the selection of suitable, highly selective solvents. Ionic liquids are deemed to be excellent solvents, because of their tunable solubility behaviour and low volatility. Castillo et al. [124] tested the use of different quaternary ammonium- and phosphonium-based ionic liquids for copper extraction. They obtained extraction efficiencies of up to 95 % for a carrier mixture of Aliquat 336 and Cyanex 272. On the other hand, Elhabiri and Didi [142] noted that the use of ionic liquids may decrease the extraction performance by approximately 50 %, based on their study on the pertraction of rare earth elements.

Next to ionic liquids, different organic ligands have been tested for MBSE- and SLM-applications. The use of specific Bz-T-DGA-ligands by Mahanty et al. [168] showed high extraction efficiencies of more than 90 % for Am(III)-extraction, although the membrane showed poor stability. On the other hand, Raut et al. [174] and Sivaramkrishna et al. [181] tested calix-crown and diamide ligands, respectively, for high level waste applications. These tests resulted in an extraction efficiency of 90 %, whilst the membrane remained stable for over 10 days. Apart from single carriers, mixtures of different carriers can also be used. Garifzyanov et al. [128] tested the use of a synergetic ligand mixture, which showed higher Li(I)-fluxes than the use of single ligands. For Ce(III)-separation, Asadollahzadeh et al. [143] used a synergetic mixture of TBP and D2EHPA, which gave higher permeation coefficients

next to an increased stability. The mixture of Cyanex 272 and D2EHPA was tested by Zaheri et al. [138] and Rajewski and Religa [148], which showed an increased performance, related to mass transport, separation factor and SLM-lifetime.

A current challenge in membrane extraction design is the solvent screening, which is based on comparative extraction experiments or previous reports in literature. However, the large amount of possible ionic liquids and organic solvents, especially if carrier mixtures are used, hampers this selection procedure [36, 194]. The addition of nanoparticles could also enhance selectivity and efficiency. Isanejad et al. [145] tested the addition of amine modified ZIF-8 nanoparticles, leading to Rhodamine B removal efficiencies up to 99.1 %, showing stability up to at least 10 hours. Tehrani and Rahbar-Kelishami [139] showed that the use of hydrophilic TiO_2-nanoparticles gave the highest permeability coefficient for gadolinium extraction. Mohammad Tehrani and Rahbar-Kelishami [140] even obtained Gd(III)- and Nd(III)-permeability coefficients 30 and 50 % higher, compared to the coefficients obtained when no nanoparticles were used.

The cycle life of a certain membrane module significantly influences the economics of the process, related to module replacement and maintenance. Based on the current literature, the stability or cycle life of a certain membrane can vary significantly. For MBSE-applications, high stabilities of up to 21 and 43 days were reached for Li(I)-extractions, by Huang et al. [101] and Xing et al. [31], respectively. Lower stabilities were reached in SLM-applications, ranging from very poor to approximately 19 days, by Mahanty et al. [168] and De Los Ríos et al. [120], respectively. De Los Ríos et al. [120] noted that after 19 days, less than 25 % of the IL was lost from the liquid membrane. Ulewicz and Radzyminska-Lenarcik [126] reported that PIMs showed a higher selectivity and stability compared to SLMs, for the separation of Cd(II), Co(II) and Ni(II). On the other hand, Baczyńska et al. [127] observed for the extraction of Zn(II), Fe(II) and Fe(III) that PIMs had a better efficiency compared to SLMs, whilst the used SLMs were more stable in consecutive

extraction and washing steps. Song et al. [131] even reported an SLM-stability of over 50 days, when a PES/SPPESK blended membrane was used for the extraction of Li(I). Therefore, SLMs can even surpass the stability of MBSE-applications and PIMs, in certain cases.

The large variation in stabilities of SLMs could be attributed to the use of different extractants. Whilst many papers report the stability issues, little attention has been awarded to possible improvements (apart from changing the extractant), even though the main instability mechanisms have already been identified in literature [27, 28]. Material selection is a critical factor in SLM-design. The current literature generally employs polymeric membranes (PP, PVDF and PTFE), which may suffer from chemical and thermal stresses, leading to membrane degradation. The use of polymer blends, such as EVAL/SPEEK, PEEK/SPEEK and PES/SPPESK, has been applied in a few cases. However, the tested applications were limited to the extraction of Li(I)- or Ni(II)-ions. Other techniques have been described to deal with stability issues, such as the use of hollow fibre renewal liquid membranes (HFRLM), in which solvent loss is avoided by constant renewal of the liquid membrane [161, 162], or polymer inclusion membranes, which are significantly more stable and robust than SLMs. On the other hand, not many papers have compared SLM-, HFRLM- and PIM-stability. SLMs could even show better performance than PIMs if many consecutive cycles are needed [39, 127]. The use of SLMs should thus not be rejected, since it still is a promising technology.

Apart from the aforementioned requirements, fouling tendency of the membrane should also be considered. Only a few papers report the fouling characteristics of the considered membranes, such as Duhamet et al. [104] and Amelio et al. [112], which could indicate that fouling is not the main challenge in membrane extraction applications. However, Castillo et al. [124] observed a fouling problem after approximately 4 hours of testing, which decreased permeability. As a countermeasure, Religa et al. [147] noted that increased stirrer speeds could reduce the effect of po-

larizing layers, which affect the mass transfer behaviour. Although Kim et al. [125] reported that membrane-based extraction systems typically do not experience fouling caused by an accumulation of particulate matter, nanoparticles could increase the fouling tendency. Mohammad Tehrani and Rahbar-Kelishami [140] showed that an increased concentration or size of the nanoparticles led to aggregation, resulting in pore blockage and decreased performance. Therefore, fouling issues should still be considered in each separation case, although the effects may be limited, when no nanoparticles are used.

Apart from fouling behaviour, solvent and membrane degradation should be considered, especially in a highly radioactive environment. Raut et al. [174] found that the solvent used for cesium-recovery, namely BOCMC, was stable towards radiolytic degradation. On the other hand, Singh et al. [180] noted that the solvent Aliquat 336, which was used for the extraction of plutonium, should be tested for chemical and radiolytic stability in further studies. For radionuclide separations, only two membrane materials were used, namely PP and PTFE. Schulze et al. [196] and Otaguro et al. [197] have reported deterioration of the mechanical properties of PP, when dosed with ionising radation (such as β- or γ-radiation). On the other hand, Ansari et al. [198] and Kandwal et al. [199] a.o. reported that polypropylene hollow fibres showed good radiation stability up to a dose of 500 kGy. Therefore, they can be used safely for radionuclide separations without significant deterioration of the performance. Similarly for PTFE, Pugmire et al. [200] and Mohammadian-Kohol et al. [201] a.o. showed an increase in stiffness and decreased tear resistance of PTFE-sheets, when dosed with γ-radiation. This implies degradation of the membrane, which increased with higher temperatures. Still PTFE is a conventional material used for radionuclide separations, with reported stabilities of up to 20 days by Raut et al. [174], which could indicate that radiolytic degradation of PTFE-membranes is only limited.

5 MEMBRANE-BASED *IN-SITU* PRODUCT REMOVAL IN CHIRAL AMINE SYNTHESIS

The biocatalytic asymmetric synthesis of chiral amines, also referred to as biocatalytic transamination, is considered a key tool in the production of a range of pharmaceuticals, such as the Alzheimer's drug rivastigmine, the adrenergic antagonist dilevalol and the antiretroviral drug lopinavir [202, 203]. Chiral amines are important building blocks for the chemical and agrochemical industries, because of its excellent enantioselectivity, as well as its green credentials [202, 204]. Challenges do remain, however, when it comes to obtaining high yields and productivity. Transaminases, also known as aminotransferases, are enzymes capable of producing these chiral amines. They catalyse the transfer of an amine group from an amine donor (typically an amino acid or a simple amine) to a pro-chiral ketone, yielding a chiral amine and a co-product ketone or an α-keto acid, as shown in Figure 4. To perform this catalysis, the transaminase enzyme typically requires a co-factor pyridoxal phosphate (PLP), which acts as a shuttle for the transfer of the amine group. This co-factor is fully regenerated within the two subsequent surface reactions on the same enzyme. Due to their stereoselectivity and ability to operate under environmentally mild conditions, transaminases are deemed suitable catalysts for the production of chiral amines [202].

Two general strategies may be applied to obtain a certain target chiral amine: direct asymmetric synthesis or kinetic resolution of a racemic amine. While the latter is often used in industrial applications today, this strategy is hampered by a theoretical yield of only 50 %, unless a racemization step is used to enable a dynamic kinetic resolution [202]. On the other hand, direct asymmetric synthesis is not limited by this theoretical yield, and is therefore the preferred reaction configuration [204]. However, optimizing this reaction setup is challenging due to inhibition and

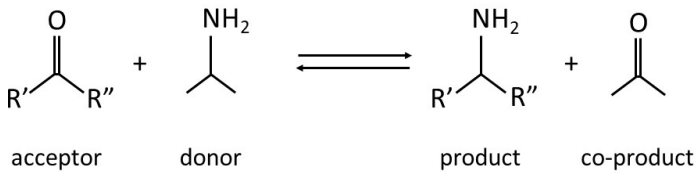


Figure 4: General overview of the biocatalytic transamination reaction. In this reaction, a transaminase enzyme is responsible for transferring an amine group from an amine donor (typically an amino acid or a simple amine) to a pro-chiral ketone, yielding a chiral amine and a co-product ketone or α-keto acid, based on [202].

stability of the biocatalyst, difficult separation of the enzyme after reaction, etc. The major challenge remains the very low equilibrium constant of transaminase reactions. A very large excess of the amine donor is needed to shift the equilibrium. Therefore, an alternative approach to push the reaction towards the products is to apply *in-situ* product removal (ISPR). Liquid-liquid extraction has been commonly used for downstream recovery of chiral amines. A drawback is that the biocatalyst's stability may be negatively affected, when contacted with certain extracting solvents. A membrane-based extraction process could then be used to prevent contacting of the enzyme and the solvent. Other possible routes for enhancing the transamination process are auto-degradation of the product, use of enzymatic cascades or employing whole-cell biocatalysis, but ISPR remains the most promising technology [202].

The use of an SLM-contactor for ISPR of MBA was first studied by Rehn et al. [204]. A reactor, containing *E. Coli* cells with ω-transaminases, was coupled to a polypropylene, hollow fibre contactor impregnated with undecane. Acetophenone and isopropyl amine (IPA) were used as the reagents for MBA-production, with acetone as the co-product. The aqueous feed of the SLM-module was kept at a high pH to ensure an uncharged amine product, which could pass into the membrane phase. If the product then entered the stripping phase which was kept at an acidic pH,

protonation occurred disallowing its transport back into the organic solvent. This "uphill" amine transport meant an increasing product concentration in the stripping phase, whilst a decrease in the feed. The ketones are not trapped in the stripping phase, but the amine donor can be co-extracted because of its own amine group. This concept is shown schematically in Figure 5. A conversion of 98 % was ultimately reached, compared to 50 % without product extraction and with 25 times excess of the donor amine. The extraction selectivity between the amine donor and product, which depends on the difference in pK_a-values and the membrane and solvent hydrophobicity, was relatively poor. Therefore, a feed pH close to the pK_a of the amine product was selected. Rehn et al. [204] concluded that a sufficiently high IPA-concentration was needed to ensure a high reaction rate, whilst avoiding an excessively high concentration to limit IPA-concentration in the strippant.

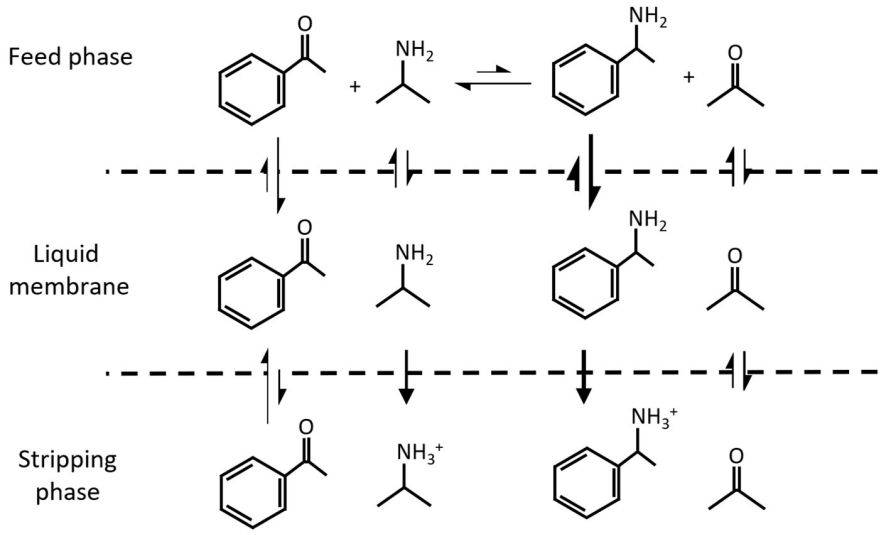


Figure 5: A schematic representation of the chiral amines extraction using an SLM, impregnated with the organic solvent. The feed and stripping phase were kept at alkaline and acidic conditions, respectively. This ensured the amine product to pass through the membrane phase, whilst back extraction was prevented by protonation of the product in the acidic strippant. The figure is based on [204].

A follow-up study by Rehn et al. [205] discussed the different factors influencing the SLM-performance. In addition, they used a continuous pH-control of the feed and a strong acidic stripping phase to ensure high product accumulation. It was

found that a higher feed pH resulted in a higher extraction rate, but a lower selectivity. On the other hand, the transaminases show a maximum activity at an optimal pH between 8 and 9. Therefore, the feed pH should be selected by a trade-off of selectivity, extraction rate and enzyme activity. The SLM was regenerated every 22 to 24 hours, but its stability could be improved by using a more viscous and hydrophobic solvent, by gelation of the LM or by employing a coating layer. However, many solvents having excellent extraction properties are insufficiently stable as a liquid membrane, and vice versa. Lastly, Rehn et al. [205] stated that an increased membrane size led to higher extraction rates, but lower purities. Again a trade-off is needed for membrane size selection.

Börner et al. [206] studied a similar system, but combined with the use of enzyme cascades. The production of 1-methyl-3-phenylpropylamine (MPPA) was studied starting from benzylacetone and alanine. The use of alanine led to a number of advantages over IPA. The co-extraction of alanine was prevented, because it shows a negative charge at high pH, disallowing its transport into the membrane. By using alanine, higher maximum extraction rates and purities were achieved, whilst avoiding (co-)product inhibition. Additionally, a broader range of transaminases could be used. However, lower conversions were reached, due to the lower equilibrium constant. By removing the co-product pyruvate via an enzyme cascade, the reaction rate could be improved. A further study by Heintz et al. [207] checked the use of a continuous, two-step LLE-configuration for ISPR of MPPA. In the first step, MPPA was extracted from the alkaline feed, whilst the second step resulted in the stripping of MPPA into the acidic strippant phase. A high purity of up to 70 % MPPA was achieved, whilst the recovery was up to 80 %. Compared to the traditional batch or fed-batch operations, a continuous operation thus enables higher purities.

Satyawali et al. [208] used an MBSE-setup, as opposed to an SLM-configuration, for the production of MPPA from benzylacetone and IPA. The transamination reaction occurred in an organic phase, which was contacted with the strippant through

a polypropylene, hollow fibre contactor. The enzyme remained stable for at least 90 hours in the organic phases, which were *n*-heptane, toluene and MTBE. Since the substrates had a higher solubility in the organic phase, higher excesses could be used, leading to higher reaction rates. Furthermore, the stability issues related to the use of a LM were avoided. Due to the hydrophobicity of the used solvents, low conversions were achieved. Only after 72 hours and at high enzyme concentrations, a substrate conversion of 99 % was reached for *n*-heptane. A disadvantage of this setup is the need for an extra nanofiltration unit to remove the co-extracted IPA. A second study by Satyawali et al. [209] detailed the use of pervaporation for *in situ* removal of the co-product acetone during MBA-production. No loss of the donor (IPA) and product amine (MBA) was observed during the pervaporation process. However, an unwanted loss of the substrate acetophenone occurred. After 9 hours of operation, a 13 % increase in productivity was found, compared to the base case without pervaporation. As a conclusion, Satyawali et al. [209] noted that the coupling of pervaporation with an SLM-setup, might enhance the productivity, since both ISPR and IScPR can occur simultaneously.

To solve the problem of co-extraction of the donor amine, Matassa et al. [210] proposed the use of high molecular weight (HMW) amine donors instead of IPA. The used setup consisted of a reaction tank which is coupled to a nanofiltration unit. The HMW amine donors are supplied in excess to shift the equilibrium further towards the reaction products. These compounds are then physically separated from the chiral amine product by the nanofiltration membrane via a size exclusion mechanism. By retention of the amine donor, combined with product removal, the conversion increased by 25 %. Limitations of this technology include a fewer selection of transaminases, since they need to be compatible with the HMW donors, and an undesirable loss of the ketone substrate and product to the permeate. The authors suggested a combination of a nanofiltration and an SLM-unit to allow for the removal of the chiral amine product without extracting the ketones.

Ferrandi and Monti [203] published a review paper discussing various ISPR-methods, including mild vacuum distillation with a nitrogen sweep for co-product removal, liquid-liquid and liquid-solid extraction and enzyme cascade reaction systems. Furthermore, enzyme immobilization was proposed. A continuous feed stream then passes the immobilized enzymes, converting the products, which are continuously removed. This would shift the equilibrium even further to the product side. Ferrandi and Monti [203] also stated that a diversity of transaminases improved rapidly, resulting in even stabler catalysts with higher reaction rates. However, strategies to shift the equilibrium are still required for chiral amine production using transaminases. Lastly, not only chiral amines can be produced by ISPR-techniques. The ISPR-methodology is also studied for the production and *in-situ* recovery of amlodipine [211, 212], itaconic acid [213], mandelic acid [214], *n*-caproic acid [215, 216], 3-hydroxypropionic acid [217], 2-phenylethanol [218, 219, 220], biobutanol [221] and carboxylic acids [222, 223, 224], but these were not discussed in more detail. For a more in-depth study on the use of (liquid) membranes for the separation of enantiomers in general, two reviews by Fernandes et al. [225] and Gössi et al. [226] can be consulted.

Table 34: Membrane-based extraction processes for the removal of chiral amines.

Donor phase	Acceptor phase	Stripping phase	Configuration and used membranes and results	Ref.
IPA, acetophenone and PLP in aqueous borax-HCl buffer	Undecane	Aqueous citrate-HCl buffer	Hollow fibre, polypropylene membranes in an SLM-setup; by using ISPR, a conversion of 98 % was reached, compared to 50 % without product removal; a high MBA-concentration of 55 g/L was reached after 80 hours	[204]
IPA, acetophenone and PLP in aqueous borax-HCl buffer	Undecane	Aqueous citrate-HCl buffer	Hollow fibre, polypropylene membranes in an SLM-setup; using continuous reactor pH-control and regular regeneration of the SLM-unit, a high MBA-concentration of 121 g/L was reached after 91 hours	[205]
Alanine, BA, PLP, LDH and NADH in aqueous borax-HCl buffer	Aqueous citrate-HCl buffer	N/A	Hollow fibre, polypropylene membranes in an SLM-setup; a high MPPA-product purity larger than 98 % was reached; the use of alanine enables high product purities, higher extraction rates and a broader enzyme range, compared to IPA	[206]
IPA, benzylacetone and PLP in aqueous carbonate buffer	Benzylacetone in undecane	Aqueous citrate buffer	Tubular, PTFE membrane in an MBSE-extractor and -stripper; an MPPA-concentration and -purity of 26.5 g/L and 70 % was reached; the MPPA-recovery was in the range of 80 % in 20 hours	[207]

Table 35: Table 34 continued.

Donor phase	Acceptor phase	Stripping phase	Configuration and used membranes and results	Ref.
IPA, BA, PLP and ATA-v2 in *n*-heptane	Aqueous sodium citrate buffer	N/A	Hollow fibre, polypropylene membranes in an MBSE-extractor; a substrate conversion of 99 % was reached after 72 hours of operation	[208]
Benzylacetone and MPPA in a *n*-heptane solution	Aqueous sodium citrate buffer	N/A	Flat sheet, PI and hollow fibre, polypropylene membranes in an MBSE-setup; the heptane solution was in contact with the reaction solution (containing the amine donor Jeffamine ED-600), this setup enables a 6-fold higher product concentration and a product yield of 60 %, compared to 15 % without product extraction	[227]

6 CONCLUSIONS AND FUTURE PERSPECTIVES

This review discussed the use and applications of membrane-based extraction technology with a focus on supported liquid membranes (SLM). As mentioned before, membrane technology is an interesting alternative for conventional liquid-liquid extraction (LLE), since it avoids inherent drawbacks of LLE, such as emulsification problems and the need for consecutive phase separation. The main applications of membrane extraction are the recovery of metal ions and rare earth elements, industrial wastewater treatment and high level waste management in the nuclear industry. However, industrial SLM-applications are few and far between, despite its enormous industrial potential. The main challenges hindering the industrial application are difficult solvent selection, insufficient SLM-stability and a lack of scale-up studies in current literature. Therefore, it is necessary to perform further research on the topic, focussing on these aspects.

In recent years, many studies have been performed to gain more insights in membrane-based extraction technology. Most of these studies focus on the definition of the appropriate solvent, which should show high selectivity, extraction rates and stability. Ionic liquids are deemed to be excellent candidates for extraction separations, due to their tunable solubility behaviour. Currently, the solvent screening is based on comparative extraction experiments or previous reports in literature [194]. However, the large amount of possible ionic liquids and organic solvents hampers this selection procedure. Future research should consider the use of *ab initio* modelling tools (e.g. COSMO-RS) to predict extraction behaviour of a multitude of solvents, before comparative extractive experiments. Commercial software, such as COSMO-RS, can aid in the definition of a simpler selection framework. COSMO-RS (COnductor-like Screening MOdel for Real Solvents) is a quantum-chemical software package, which enables the user to implement the molecular structure of solutes and solvents. The solute-solvent affinity can then be

computed *in silico* to obtain a primary solvent selection [228]. Additionally, further research should also look into other critical solvent properties, such as feed/solvent and solvent/strip emulsification behaviour and miscibility, apart from selectivity.

Next to the selection of suitable solvents, the SLM-stability should be tackled further in research, especially related to material selection, which is a critical factor in SLM-design. Currently, polymeric membranes (PP, PVDF and PTFE) are generally employed for MBSE- and SLM-applications. These materials are prone to degradation, if suffering from chemical and thermal stresses. Polymeric blends, such as EVAL/SPEEK, PEEK/SPEEK and PES/SPPESK, have already been tested as an alternative. However, the tested applications were limited to the extraction of Li(I)- or Ni(II)-ions. Apart from polymeric membranes, an alternative is the use of ceramic membranes, which are characterised by a very high chemical, thermal and mechanical stability. The hydrophobicity of ceramic membranes, which are typically hydrophilic in nature, can be improved by surface modification. Apart from papers related to membrane modification, very few papers report the use of ceramic membranes for membrane extraction purposes, even though they could show a high potential for these applications [3, 229]. Apart from the selection of suitable materials, gelation of the LM-matrix and surface coating can be used to enhance SLM-stability. Unfortunately, these stabilization methods were not addressed much in the current literature, even though gelation of ionic liquids has already been studied extensively in the literature [2, 230]. The use of hollow fibre renewal liquid membranes (HFRLM), in which the liquid membrane is constantly renewed [161, 162], or polymer inclusion membranes, have also been proposed as alternatives for SLMs. Still, more research is needed to compare the different techniques for specific separation cases, since SLMs could even show better performance than PIMs, if many consecutive cycles are needed [39, 127].

Finally, little attention has been awarded to the design of industrial MBSE-equipment. To enable application of SLMs on an industrial scale, process optimization

and pilot-scale testing are needed. The use of modelling techniques, such as computational fluid dynamics (CFD), is an important tool for process optimization. Membrane performance can be evaluated quantitatively by determination of the overall extraction yield. In addition, the mass transfer behaviour of the membranes can be evaluated by different parameters, namely membrane permeability, solutes' fluxes and the overall mass transfer coefficient K_t. A selection of studies presents the use of CFD for determination of optimal process parameters. Despite the advantages of CFD-modelling, such as easy and fast calculations, validation is still needed via comparative extraction experiments. Unfortunately, the validation of the obtained velocity and concentration profiles is not possible, since these cannot be obtained experimentally. CFD also employs a number of assumptions, whose validity should be checked for each separation case. Next to process optimization, pilot setups are needed to allow correct upscaling of the lab-scale equipment. In 2013, Buekenhoudt et al. [231] proposed a large-scale mobile pilot installation for organic solvent nanofiltration (OSN). The installation can be equipped with ceramic and polymeric membranes. It allows for non-thermal, energy-efficient and highly selective separation and can potentially replace part of the huge number of traditional separation processes, mainly based on thermal separations. The process is not only limited to OSN, but it can be applied in other membrane processes, such as reverse osmosis (RO) and aqueous ultrafiltration (UF), but most importantly for membrane extraction purposes. A configuration as tested by Buekenhoudt et al. [231] can be used for the transition from lab-scale testing to industrial membrane extraction applications.

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CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest.

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