Solvent resistant nanofiltration: separating on a molecular level

Pieter Vandezande,[a] Lieven E. M. Gevers[b] and Ivo F. J. Vankelecom*[a]

Received 25th July 2007
First published as an Advance Article on the web 8th October 2007
DOI: 10.1039/b610848m

Over the past decade, solvent resistant nanofiltration (SRNF) has gained a lot of attention, as it is a promising energy- and waste-efficient unit process to separate mixtures down to a molecular level. This *critical review* focuses on all aspects related to this new burgeoning technology, occasionally also including literature obtained on aqueous applications or related membrane processes, if of relevance to understand SRNF better. An overview of the different membrane materials and the methods to turn them into suitable SRNF-membranes will be given first. The membrane transport mechanism and its modelling will receive attention in order to understand the process and the reported membrane performances better. Finally, all SRNF-applications reported so far – in food chemistry, petrochemistry, catalysis, pharmaceutical manufacturing – will be reviewed exhaustively (324 references).

Abbreviations

6FDA	2,2-Bis(2,4-dicarboxyphenyl) hexafluoropropane dianhydride
CA	Cellulose acetate
DCM	Dichloromethane
DEGDME	Diethylene glycol dimethyl ether
DKR	Dynamic kinetic resolution
DMA	*N*,*N*-Dimethylacetamide
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
EA	Ethyl acetate
ECTFE	Ethylene chlorotrifluoroethylene
EG	Ethylene glycol

Ivo F. J. Vankelecom

Ivo Vankelecom (Ninove, Belgium, 1967) studied Bioscience Engineering at the Catholic University of Leuven (K.U.Leuven), Belgium, where he graduated in 1990. In 1994, he obtained his PhD in Applied Biological Sciences from the Department of Interphase Chemistry on ''Inorganic Porous Fillers in Organic Polymer Membranes''. Until 2002, he worked at K.U.Leuven as a postdoc on membrane catalysis. During this period, he spent 6 months at the Ben-Gurion University of the Negev (Beersheva, Israel) and at Imperial College (London, England). Since 2002, he has been a professor at K.U.Leuven where he teaches Membrane Technology, Adsorption and Chromatography.

Pieter Vandezande

Pieter Vandezande was born in Tienen (Belgium) in 1980. He obtained his MSc in Bioscience Engineering at K.U.Leuven in 2003. He is presently working on his doctoral degree at the Centre for Surface Chemistry and Catalysis under the supervision of Prof. Vankelecom and Prof. Jacobs. His work involves the synthesis and characterization of polymers with controlled porosity and the implementation of high throughput and combinatorial techniques in membrane technology.

Lieven E. M. Gevers

Lieven Gevers was born in Duffel on June 8th 1978. He is married to Marleen Stuyck and father of Mille and Tuur. In 2001, he finished his studies on Bio-engineering Chemistry at the K.U.Leuven, Belgium. Under the supervision of Prof. Jacobs and Prof. Vankelecom he started a PhD at the Centre for Surface Chemistry and Catalysis. His research resulted in 12 publications, 2 patents and 2 chapters in books. Currently he is working at VITO as application engineer in membrane technology.

---

[a] *Centre for Surface Chemistry and Catalysis, Faculty of Bioscience Engineering, Catholic University Leuven, Kasteelpark Arenberg 23 – bus 2461, B-3001, Leuven, Belgium.*
E-mail: ivo.vankelecom@biw.kuleuven.be; Fax: +32-16-321998; Tel: +32-16-321594
[b] *Flemisch Institute for Technological Research (VITO), Boeretang 200, B-2400, Mol, Belgium*

EGME	Ethylene glycol methyl ether
FFA	Free fatty acid
GS	Gas separation
HITK	Hermsdorfer Institut für Technische Keramik
ILs	Ionic liquids
IPC	Isophthaloyl chloride
MA	Methyl acrylate
MBR	Membrane bioreactor
MEK	Methyl ethyl ketone
MF	Microfiltration
MIBK	Methyl isobutyl ketone
m-PDA	*meta*-Phenylene diamine
MSBE	Membrane based solvent back extraction
MSE	Membrane solvent extraction
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NMP	*N*-Methylpyrrolidinone
o-PDA	*ortho*-Phenylene diamine
OSN	Organic solvent nanofiltration
PA	Polyamide
PAA	Polyacrylic acid
PAH	Poly(amide hydrazide)
PAI	Poly(amide imide)
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
PDMS	Polydimethylsiloxane
PEA	Poly(ether amide)
PEAH	Poly(etheramide hydrazide)
PEBAX	Poly(ethylene oxide-*b*-amide)
PEEK	Poly(ether ether ketone)
PEi	Poly(ethylene imine)
PEI	Poly(ether imide)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PES	Poly(ether sulfone)
PI	Polyimide
PIB	Polyisobutylene
p-PDA	*para*-Phenylene diamine
PPESK	Poly(phtalazinone ether sulfone ketone)
PPO	Poly(2,6-dimethyl-1,4-phenylene oxide)
PPO-Br	Brominated poly(2,6-dimethyl-1,4-phenylene oxide)
PPSf	Poly(phenylene sulfone)
PPz	Polyphosphazene
PSf	Polysulfone
PS	Polystyrene
PTCs	Phase transfer catalysts
PTMSP	Poly[1-(trimethylsilyl)-1-propyne]
PU	Polyurethane
PUA	Poly(urea amide)
PV	Pervaporation
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
RO	Reverse osmosis
S-*m*-PDA	*meta*-Phenylene diamine-5-sulfonic acid
SEM	Scanning electron microscopy
SPEEK	Sulfonated poly(ether ether ketone)
SPPESK	Sulfonated poly(phtalazinone ether sulfone ketone)
SPPO	Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)
SRNF	Solvent resistant nanofiltration
TFC	Thin film composite
THF	Tetrahydrofuran
TIPS	Thermally induced phase separation
TMC	Trimesoylchloride
TOABr	Tetra octyl ammonium bromide
TPC	Terephthaloyl chloride
UF	Ultrafiltration
XPS X-ray	Photoelectron spectroscopy

Nomenclature

$a_{1,0}$	activity of solvent in feed side of membrane
$a_{2,0}$	activity of solute in feed side of membrane
$a_{1,\ell}$	activity of solvent in permeate side of membrane
$a_{2,\ell}$	activity of solute in permeate side of membrane
C	molar density of the mixture [mol m^{-3}]
C_i	molar concentration of species i [mol m^{-3}]
c_2	solute concentration [mol m^{-3}]
$\bar{c}_2$	($=\Delta c_2/\Delta \ln c_2$) logarithmic average of solute concentration across the membrane [mol m^{-3}]
Δc_2	concentration difference of solute across the membrane [mol m^{-3}]
C^S_{20}	solute concentration upstream solution [mol m^{-3}]
$C^\mathrm{S}_{2\ell}$	solute concentration downstream solution [mol m^{-3}]
C^m_{20}	solute concentration in membrane at the side facing the upstream solution [mol m^{-3}]
$C^\mathrm{m}_{2\ell}$	solute concentration in membrane at the side facing the downstream solution [mol m^{-3}]
D_0	diffusion coefficient solute in pure solvent, calculated by Wilke Chang [m^2 s^{-1}]
D_1m	multi component diffusion coefficient of solvent *versus* membrane [m^2 s^{-1}]
D_2m	multi component diffusion coefficient of solute *versus* membrane [m^2 s^{-1}]
D_{12}	multi component diffusion coefficient of solute *versus* solvent [m^2 s^{-1}]
F	Faraday constant [96487 C mol^{-1}]
J_solvent	volume flux for solvent [m^3 (m^2 s)$^{-1}$]
J_1	molar solvent flux [mol s^{-1} m^{-2})]
J_2	molar solute flux [mol s^{-1} m^{-2})]
J_v	volume flux [m s^{-1}]
K_1	solvent sorption [mol solvent m^{-3} membrane]
K_2	solute distribution coefficient [(mol m^{-3} membrane) (mol m^{-3} solution)$^{-1}$]
$K_\mathrm{2,c}$	hindrance factor for convection
$K_\mathrm{2,d}$	hindrance factor for diffusion
L_p	mechanical filtration coefficient [m s^{-1} bar^{-1}]
ℓ	membrane thickness [m]
M_1	molar weight of solvent [Da]
M_2	molar weight of solute [Da]
n_1	mass flux of solvent [g (m^2 s)$^{-1}$]
n_2	mass flux of solute [g (m^2 s)$^{-1}$]

p_0	pressure upstream solution [Pa]
p_ℓ	pressure downstream solution [Pa]
P_2	solute permeability [$\mathrm{m^3\ (m^2\ s)^{-1}}$]
p_0	pressure upstream solution [Pa]
p_ℓ	pressure downstream solution [Pa]
ΔP	pressure difference [Pa]
r_s	solute radius [m]
r_p	pore radius [m]
R	gas constant = 8.31451 [$\mathrm{J\ (K\ mol)^{-1}}$]
T	temperature [K]
$\bar{V}_1$	molar volume solvent [$\mathrm{m^3\ mol^{-1}}$]
$\bar{V}_2$	molar volume solute [$\mathrm{m^3\ mol^{-1}}$]
v_i	diffusive volume flux of a species i [$\mathrm{m\ s^{-1}}$]
w_{10}	mass fraction of solvent in membrane at the upstream side [$\mathrm{g\ g^{-1}}$]
$w_{1\ell}$	mass fraction of solvent in membrane at the downstream side [$\mathrm{g\ g^{-1}}$]
$\bar{w}_1$	$= \dfrac{w_{10}+w_{1\ell}}{2}$
w_1^*	mass fraction of solvent in membrane at equilibrium swelling [$\mathrm{g\ g^{-1}}$]
w_{20}	mass fraction of solute in membrane at the side facing the upstream solution [$\mathrm{g\ g^{-1}}$]
$w_{2\ell}$	mass fraction of solute in membrane at the side facing the downstream solution [$\mathrm{g\ g^{-1}}$]
$\bar{w}_2$	$= \dfrac{w_{20}+w_{2\ell}}{2}$
$\bar{w}_\mathrm{m}$	$= \dfrac{w_{10}-w_{1\ell}}{\ln\left(\dfrac{(1-w_{1\ell})}{(1-w_{10})}\right)}$
x_i	molar fraction of species i in membrane
x_1	molar fraction of solvent in membrane; x_2 molar fraction of solute in membrane
Δx	top-layer thickness [m]
z_i	valence of electrolyte

Greek symbols

π_0	osmotic pressure upstream solution [bar]
π_ℓ	osmotic pressure downstream solution [bar]
$\Delta\pi$	osmotic pressure difference across the membrane [bar]
ρ	mass density of the membrane [g membrane/$\mathrm{m^3}$ membrane)]
ε_1	$= \dfrac{D_{1\mathrm{m}}}{D_{12}}$ frictional coupling coefficient
ε_2	$= \dfrac{M_2}{M_1}\cdot\dfrac{D_{2\mathrm{m}}}{D_{12}}$ frictional coupling coefficient
σ	reflection coefficient and P is the solute permeability [$\mathrm{m\ s^{-1}}$]
ψ	electric potential [V]
$\varphi(r)$	potential function of force exerted on solute by the membrane material [$\mathrm{J\ (g\ mol)^{-1}}$]
$\varsigma_{1,2}$	frictional coefficient between solute and solvent [$\mathrm{J\ s\ (m^2\ g\ mol)^{-1}}$]
$\varsigma_{2,3}$	frictional coefficient between solute and membrane material [$\mathrm{J\ s\ (m^2\ g\ mol)^{-1}}$]
ε	porosity
η	solution viscosity [$\mathrm{kg\ (m\ s)^{-1}}$]
τ	tortuosity

1 Introduction

The field of membrane separations is typically interdisciplinary, involving materials science and engineering, chemical synthesis and characterization of membrane materials, membrane manufacturing and modification, module design, process engineering, integration of membrane processes in industrial processes as well as economical, ecological and safety issues. Today, the growth of membrane technology is based on technical achievements, the steadily growing acceptance in various industries, energy prices and environmental concerns. The membrane industry itself has a profound perspective as illustrated by its growth rate, the increasing diversity of applications, and the growing number of technically feasible membrane processes.

Whenever selectivity in membrane filtrations is based on size-exclusion, it is easily understood that smaller pores are able to reject smaller molecules. The picture gets more complicated when membranes separate on a molecular level. This is where liquid-phase pressure-driven membrane processes have been referred to in literature as nanofiltration (NF), a term 'invented' during a Filmtech meeting in 1984,[1] or reverse osmosis (RO), or sometimes even ultrafiltration (UF). The terminology is however not well-defined. An operational definition classifies the processes according to the pressure required to create the necessary driving force for the membrane separation: pressures for UF normally range from 1 to 5 bar, for NF from 5 to 20 bar and for RO from 10 bar upwards.[2] The 1996 IUPAC-nomenclature on the other hand, distinguishes the processes according to the size of the retained solute. RO is defined as a process in which only solvents permeate, while particles and dissolved molecules smaller than 2 nm are rejected in NF, and compounds between 2 nm and 0.1 μm in UF.[3] Strictly spoken, these definitions would imply that the very same membrane operated at 4 or 6 bar or in a strongly swelling or non-swelling solvent, would have to be referred to as an UF- or NF-membrane respectively, depending on the conditions. With such blur borderline, these three liquid-phase pressure-driven membrane processes will be covered in this review without distinction. Since only applications in organic solvents will be considered, the term solvent resistant nanofiltration (SRNF) will be used for their general description. Organic solvent nanofiltration (OSN) is the alternative nomenclature regularly found in the literature.

Even though pressure-driven solvent separations had been occasionally mentioned already, for instance in 1965,[4] SRNF is a relatively young technology that broke through around the beginning of this century. Hence, it can not be considered a proven technology yet, but surely holds enormous potential as it allows separations of organic mixtures down to a molecular level by simply applying a pressure gradient over a membrane. In this range of membrane filtrations where discrimination occurs at molecular level, mutual interactions between solute and solvent, solvent and membrane, as well as between solute and membrane start to play a key role in addition to – and often even more dominant than – mere molecular size. It makes SRNF less accessible for the non-specialist, and renders selection of a suitable membrane type for a given separation relatively difficult. The latter is even more complicated when commercially available membranes are considered whose physico-chemical properties are seldom known.

The review will start with some general SRNF-specific issues, after which the most important membrane materials applicable for SRNF, as well as their properties and synthesis procedures will be discussed. A special section will feature the main commercial SRNF-membranes. To increase the chances for proper membrane selection anyhow, a further chapter will be dedicated to membrane transport mechanisms, and – coinciding with it to a certain extent – transport modeling. Since good SRNF-membranes are commercially available these days and many others have been 'tailor-made' for specific purposes, a large chapter will focus on all applications studied so far – summarized per industry branch. A chapter about upscaling and module design, and a general outlook of the field will conclude this review.

Since some NF-membranes developed for aqueous applications are resistant in numerous solvents in which they might even show good rejections for certain solutes, the borderline between membranes for aqueous applications and solvent applications is very diffuse for polymeric membranes. The same surely holds for ceramic membranes that will obviously neither dissolve nor swell even slightly in any organic solvent. For this reason several references that in fact deal with aqueous applications have been included in this review, as well as references dealing with related membranes such as gas separation (GS) membranes, whenever they contributed in our opinion to the general better understanding of SRNF.

2 General considerations

2.1 Advantages and disadvantages of SRNF

The general main incentives to apply SRNF are numerous. In most cases, no additives are needed, and separations don't involve any phase transition. Thermal damage, resulting in degradation and side reactions, can be minimized during the separation due to the low temperature of operation compared with distillation. Possibilities are created to recycle solvents and/or valuable compounds and to lower losses or exhausts. Energy consumption is low as compared with alternative unit operations like distillation and crystallization. Athermal solvent exchanges can be performed, allowing to swap from a high-boiling to a low-boiling solvent. SRNF can be installed easily as a continuous process, and just like any other membrane separation, it can be combined readily with existing processes into a hybrid process. The latter can be attributed to its modular set-up, which also renders upscaling relatively simple.

Despite these clear advantages, only few large-scale SRNF-processes are running yet, even though many pilot-scale tests currently seem to be on-going.[5] In addition to the general reluctance of the chemical industry to implement new technologies, one of the main reasons for the delayed breakthrough is probably a lack of robustness of the membranes. The main challenge for the further expansion of SRNF thus remains the development of membranes that are stable in a wide range of organic solvents, and show high and reproducible performances on the long term, combining elevated solvent permeabilities and acceptable rejections for molecules in the 200–1000 g mol^{-1} molar mass range. The stability demands for the membrane can indeed be really tough in non-aqueous and sometimes even reactive environments with high-temperature processing. Even if sufficiently stable, the right membrane (*i.e.* combining a sufficient selectivity with an acceptable flux) for a given separation problem might not be available yet, or – at least as important – the process manager involved might simply not be aware of its existence. Finally, for large-scale applications, membrane fouling and concentration polarization remain important issues, which have so far been addressed much less for organic feeds than for aqueous. Membrane feed boundary layer phenomena are indeed of extreme importance to establish correct long-term filtrations and to get the maximum performance out of a membrane.

2.2 Practical issues in SRNF

2.2.1 Separation performance of SRNF-membranes. The performance of a given membrane is determined by two parameters: selectivity and flow. The latter, generally denoted as flux or permeation rate, is defined as the volume liquid flowing through the membrane per unit area and per unit time, and is generally expressed as l/(m^2 h), while permeabilities (l/(m^2 h bar) are normalized to the applied pressure. Rejections (%) are mostly calculated as $(C_p - C_f)/C_p$, where c_f and c_p denote the analyte concentration of feed and permeate, respectively. In addition, the separation performance of a membrane can also be expressed by its 'molecular weight cut-off' (MWCO). This represents the molecular weight (MW) corresponding to a reference compound that is typically retained for 90%. The MWCO can be derived from a MWCO-curve, featuring the membrane's rejection for analytes with increasing MW. NF-membranes typically show MWCOs in the 200–1000 Da range.

Although SRNF-membranes have meanwhile been applied and investigated by multiple authors, literature data tend to be rather application-specific and thus hardly comparable. The specific properties of the used solvents and solutes (structure, size, charge, concentration, *etc.*), as well as the experimental filtration conditions (transmembrane pressure, temperature) applied in most studies, make filtration data, including MWCO-values, of different experiments hardly comparable. The changing characteristics of a certain solute in different solvents have to be considered when interpreting filtration data. This change holds first of all for the molecular shape. Oligomeric forms of polyisobutylene (PIB),[6–9] poly(ethylene glycol) (PEG)[10,11] or polystyrene (PS),[9] all popular solutes to determine MWCO-curves in solvents, are solvated to different extents and can change from almost globular shape to extended coils. Second, charges can be shielded better or worse in organic solvents with low or high dielectric constants respectively. Third, cluster formation of solutes can appear in relatively bad solvents or from certain concentrations onwards.[12] Furthermore, even if filtration conditions would exactly match, rejections determined with different analytical techniques, often not clearly disclosed, could differ. Due to this non-uniformity, the selection of a suitable membrane for a given application often necessitates the screening of many membranes. As membrane selection for SRNF-applications is often based on literature-given or manufacturer-specified

MWCO-values (often still measured in aqueous environments), a clear need exists to develop a consistent and universal method to characterize the performance of SRNF-membranes. A first step in that direction has recently been set using a homologous series of styrene oligomers spanning the NF-range and well soluble in methanol, ethyl acetate (EA), hexane and toluene.[13]

2.2.2 Filtration conditions, system design and mass transfer limitations. Apart from the variability in the characterization of SRNF-membranes, the way filtration data are collected varies widely as well. The majority of SRNF-applications reported in literature have been obtained on lab-scale set-ups in dead-end filtration mode (Fig. 1a), while industrial membrane applications generally run in cross-flow mode (Fig. 1b). In dead-end, the feed is forced through the membrane by a pressure perpendicular on the membrane surface, whereas in cross-flow, the feed flows parallel to the membrane surface, as schematically shown in Fig. 1. The short-term performances reported by academic groups, mostly obtained in dead-end mode, will not necessarily be reproducible in long-term testing or under cross-flow conditions. Furthermore, the module configuration in which the membrane is packed has a profound influence on its performance. In academic studies, flat sheet membranes (seldom applied in a module) are generally used, occasionally also spiral-wound modules, while the latter module type is the most popular in industrial applications. Therefore, wherever in this review reference is made to performance data, particularly in the applications section, the conditions under which data are collected will be indicated between square brackets. This will allow the reader to get some idea about the reliability/quality of the data. The system design will be indicated as DE (dead-end), CF (cross-flow) or CU (conditions unknown), while the length of the filtration test will be denoted as either S (short, less than 10 hours) or L (long, more than 10 hours). Mostly flat sheet membranes are used, unless indicated differently as SW (spiral-wound) or HF (hollow fiber), and the operational strategy (batch, continuous or diafiltration) will also be indicated where possible. For upscaling and industrial implementation, with special emphasis on module configurations, system design and operational concepts will be discussed in more detail in paragraph 6.

In contrast to cross-flow filtrations, dead-end filtrations involve pressurization of the feed with a gas. The role of the pressurizing gas solubility in the feed, and of the expansion of this dissolved gas while going from the feed pressure to the atmospheric permeate pressure during membrane permeation, have not been formally studied yet. The better feed hydrodynamics in cross-flow filtrations will generally induce higher fluxes, but the overall effect is rather unpredictable since concentration polarization might lower selectivity, while fouling phenomena, like cake-layer formation or solute adsorption on the membrane surface, generally increase selectivity. Fouling is defined as the process resulting in loss of membrane performance due to the deposition of suspended or dissolved substances on its external surface, at pore openings, or within pores.[2,3] Concentration polarization is an important fouling mechanism, referring to the accumulation of retained solutes at the membrane boundary layer. It creates a higher solute concentration at the membrane surface compared with the bulk solution. This boundary layer concentration is critical for flux and rejection and might induce further fouling. The increased osmotic pressure of retained compounds and the possible formation of a gel-layer reduce fluxes and complicate interpretation of rejection values. Membrane fouling is mostly a reversible process that can be controlled by several technical modifications, such as increasing cross-flow velocity, permeate pulsing and ultrasound treatment.[14]

Important flux losses can also be caused by increasing retentate concentrations during the course of a small-scale batchwise filtration. Being either roughly estimated by the Van 't Hoff equation, or calculated from extrapolations to zero flux on pressure–flux plots, osmotic pressures $\Delta\pi$ in the retentate can increase substantially this way, hence drastically lowering the actual driving force ($\Delta P - \Delta\pi$). Additionally, the above-mentioned concentration polarization and fouling phenomena might become even more prominent. More fundamental research is certainly needed on the Van 't Hoff equation to prove its applicability in organics solvents.[15] Non-ideality of tetraoctylammonium bromide (TOABr) in toluene for instance has been reported already and explained by ion-pair clustering of the TOABr molecules.[16] On the other hand, sunflower oil behaved ideally in the same solvent,[16] just like PIB in hexane and toluene.[6]

In contrast to aqueous NF, mass transfer-limiting phenomena at the membrane–feed solution interface have hardly received any attention yet in SRNF and most results have been obtained on small lab-scale dead-end filtration set-ups. The few studies however are quite encouraging.[16–19] Studying feeds with up to 30 wt% dissolved organics, the observed flux and rejection trends could be described accurately by the suggested model when non-ideality of activity coefficients was implemented. Lab-scale data obtained

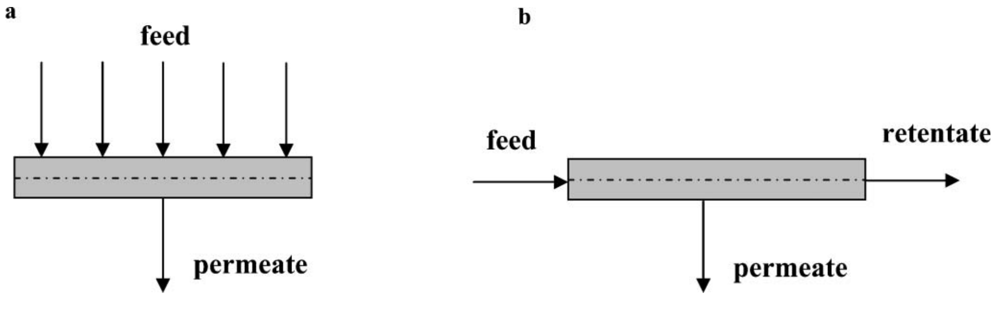


Fig. 1 Schematic representation of membrane filtration system design: (a) dead-end, (b) cross-flow mode (adapted from ref. 2).

with small flat sheet coupons were found to correlate well with the results obtained using larger spiral-wound modules, especially when obtained under cross-flow instead of dead-end conditions.[18]

Another important aspect of short-term lab-scale filtrations is an often solvent dependent compaction of polymeric SRNF-membranes, observed as a severe initial flux decline during the experiment. This phenomenon which has been observed by many authors[17,20,21] can be ascribed to a rearrangement of (partly solvated) polymer chains under the applied pressure.[20] The time needed for the membrane flux to reach complete equilibrium depends on many conditions, but can easily be as long as several days and is highly dependent on membrane pretreatment.[22]

2.2.3 Membrane conditioning. Another major source of variability or 'incomparability' between performances of identically synthesized SRNF-membranes is related to the post-synthesis conditioning of the membranes. This involves the storage of the membrane from its moment of synthesis till its actual application, including 'membrane rinsing' in the filtration cell prior to contacting the membrane with the actual feed stream to be filtered. Inappropriate conditioning can make a superior membrane loose all of its performance. Defining appropriate storage and rinsing conditions is not easy and gets more complicated with many commercial membranes whose membrane structure and composition are unknown. No doubt many good membrane/solvent/solute combinations have been discarded in the past due to such membrane 'mistreatment'. The pores of membranes prepared *via* phase inversion (see below) for instance are filled with the coagulation bath solution right after synthesis. Removing this solvent, *e.g.* *via* extended air contact, would make the smallest pores collapse due to capillary forces, especially with liquids of high surface tension like water. Precisely these small pores are crucial in determining membrane flux and selectivity, as they are primarily present at the membrane top-surface or realize the interconnectivity between the larger pores. Conditioning agents are typically used to keep the smallest membrane pores open during handling. Examples are lubricating oils and glycerol, dissolved in apolar and polar solvents, for subsequent filtrations of apolar or polar feeds respectively.[23,24]

The presence of the conditioning agent in the pores after membrane preparation often allows evaporation of the solvents and thus dry membrane storage, since the remaining oil or glycerol prevents the pores from collapsing. In order to avoid pore obstructions and concomitant lowered fluxes, the conditioner should obviously be removed carefully with an appropriate solvent prior to application.[24,25] Once the conditioning agent has been removed, the membranes should never be left dry without re-introduction of the conditioner. Only membranes with a dense rubbery top-layer supported by a layer with sufficiently large surface pores, can be stored dry without many precautions. However, the main risk for pore collapse at the level of the support is situated here during the application of the top-layer *via* solvent casting.[24,26,27]

3 Membrane preparation

3.1 Introduction

The material selection for SRNF-membranes can be based on the following characteristics: film forming properties, chemical and thermal stability, commercial availability and price, and affinity for the components in the feed. For food and pharmaceutical applications, reliable purity grades and FDA-approval of materials, membranes, and modules are required. Upscaling and industrial implementation generally require reproducible membrane performances as well as long-term stability and cleanability. In terms of chemical, thermal and structural stability, ceramic membranes are obviously superior. They do not deform under pressure, do not swell and are cleaned easily. Their large-scale synthesis and module construction may however be complicated, they tend to be more expensive and brittle than polymeric membranes and are also less versatile in applications. In contrast to polymeric membranes, ceramic SRNF-membranes are still much less widespread, even though significant progress in this field has been made recently.

Phase inversion, developed by Loeb and Sourirajan[28] in the early sixties, represents one of the most versatile, economical and reproducible formation mechanisms for polymeric asymmetric membranes. These membranes possess a skin-layer on top of a more porous sublayer with the same composition (Fig. 2a). Due to their low manufacturing costs, integral asymmetric membranes dominate a significant part of the membrane market for water treatment.[2,29] The key for high performance is the very thin skin-layer which enables a high selectivity and permeability. Another important class of membranes, useful for RO and NF, are thin film composite (TFC) membranes, exhaustively reviewed by Petersen[30] and consisting of an ultra-thin (submicron) separating 'barrier' on top of a chemically different porous support (Fig. 2b). The separating layer of TFC membranes for aqueous applications is usually prepared *via* dip-coating or by interfacial polymerization on a

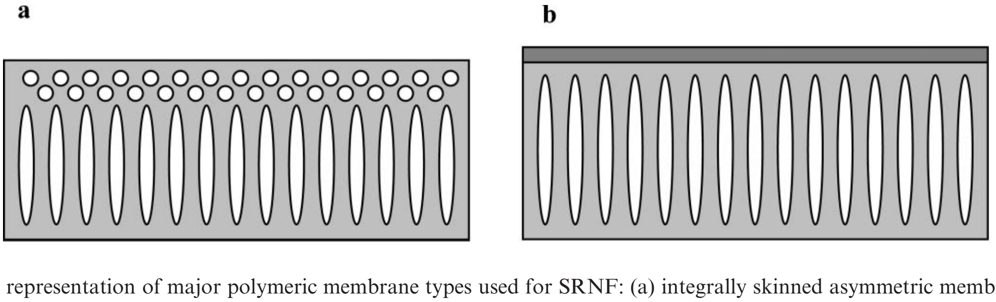


Fig. 2 Schematic representation of major polymeric membrane types used for SRNF: (a) integrally skinned asymmetric membrane, (b) thin film composite (TFC) membrane.

support-layer usually prepared *via* phase inversion. Due to their layered structure, TFC membranes are very flexible as the chemistry and performance of both barrier-layer and porous substrate can be independently optimized to maximize the overall membrane performance.[2,29,30]

This chapter will cover all synthesis techniques applied for SRNF-membranes, polymeric as well as ceramic membranes, starting with a concise description of the underlying principles when needed, followed by more specific examples. Some general aspects of support-layers for composite membranes will be discussed first. Reference will often be made to the preparation of NF-membranes for aqueous applications, studied already in much more detail, to help explain the effect of certain parameters. The chapter will be concluded with a description of the synthesis, performance and/or composition of the most common commercial SRNF-membranes. A more detailed review on NF-membrane preparation for both aqueous and solvent applications has recently been published.[31]

Membrane synthesis often involves such complex mixtures of polymers, solvents and additives that compositional optimization for a given target separation becomes extremely difficult and time-consuming, if not impossible *via* a conventional parameter-by-parameter approach. New methods involving Design of Experiments, such as combinatorial synthesis, seem to be ideal in this respect to discover the optimal composition of the polymer solution. This has been proven already for a polyimide (PI) based SRNF-membrane prepared *via* phase inversion and optimized using genetic algorithms.[32] The optimal casting composition, involving 8 different compounds, led to a three-fold improved flux/selectivity combination as compared to the best available commercial membranes (Fig. 3). As such optimization needs preparation and testing of many samples (typically about 200 different membranes), high throughput membrane synthesis and testing equipment, as developed recently, is almost essential.[33]

3.2 Supports

The choice of the support-layer for composite SRNF-membranes is important as it should provide mechanical stability and allow application of thin and defect-free top-layers (Fig. 4). Its mechanical, chemical and thermal properties should meet the criteria imposed by the separation, while its surface roughness and polarity determine the adhesion between both layers under filtration conditions. Often, the support itself is still applied on a substrate, commonly a polyester or polypropylene/polyethylene nonwoven backing, to enhance mechanical strength and handling.[2,30] Asymmetric microporous polysulfone (PSf) membranes are frequently used supports. However, since PSf is sensitive to certain solvent classes, the choice of the contacting solvents during top-layer deposition is rather limited.[30] Other more stable UF-supports have been mentioned in literature – mostly in an aqueous NF-context but possibly suitable for solvent filtrations as well – including poly(ether sulfone) (PES),[34] polyacrylonitrile (PAN),[35] poly(vinylidene fluoride) (PVDF)[36] and polypropylene (PP),[37,38] PI,[24] PAN[39] and polybenzimidazole (PBI)[40] as well as inorganic membranes.[41]

A sufficiently strong binding between the support and the top-layer is not trivial and can cause stability problems on the long term, reflected in top-layer peel-off, especially under conditions of excessive top-layer swelling. The formation of an interpenetrating layer of the active layer inside the pores of the support has been suggested to strengthen the interaction.[30] However, excessive penetration in the support will make this membrane part become rate-limiting, hence significantly reducing the membrane flux.[42] The problem of top-layer

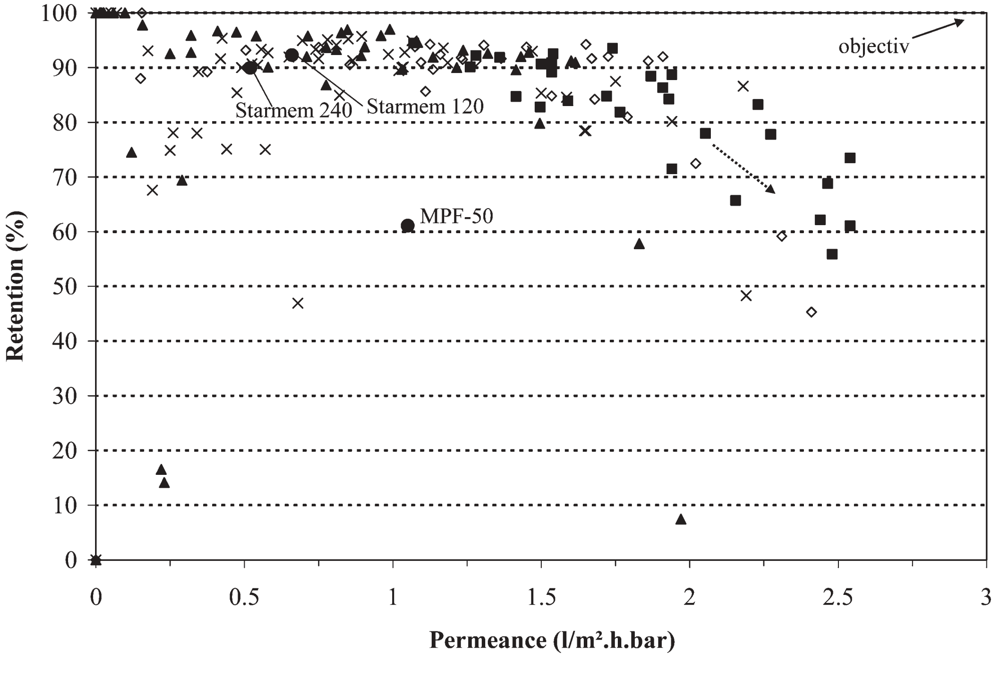


Fig. 3 Performances of the 4 generations (▲: 1st generation; ×: 2nd generation; ◇: 3rd generation; ■: 4th generation) in the combinatorial optimization of PI-based SRNF-membranes in an 8-dimensional compositional parameter space. Separation of methyl orange (327 Da) from *i*-propanol at 10 bar and rt [DE-S] (taken from ref. 32).

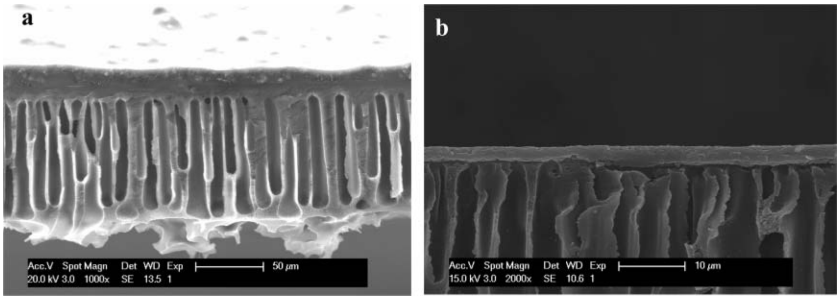


Fig. 4 SEM-images of TFC membranes: (a) zeolite-filled PDMS top-layer coated on a microporous PI support, (b) PA top-layer interfacially polymerized (see 3.4.) on a PI support.

intrusion can be reduced by filling the pores of the support with a solvent.[24]

3.3 Phase inversion

3.3.1 Basic principles. 'Phase inversion' refers to the controlled transformation of a cast polymer film from a liquid to a solid state. During this process, a thermodynamically stable polymer solution is mostly subjected to a controlled liquid–liquid demixing during which the cast polymer film 'phase-separates' into a polymer-rich and a polymer-lean phase, ultimately forming the matrix and the pores of the membrane, respectively. This phase separation can be induced by immersing the film in a non-solvent bath ('immersion-precipitation'), by lowering the temperature ('thermal precipitation'), by evaporating the volatile solvent from the polymer film ('controlled evaporation') or by placing the cast polymer film in a non-solvent vapour phase ('precipitation from the vapour phase').[2,29,31,43] A 'non-solvent' in this context refers to a relatively bad solvent for the polymer. This chapter will mainly focus on asymmetric membranes obtained *via* immersion-precipitation, which is the most common phase inversion method.

The thermodynamic behaviour of a polymer solution subjected to immersion-precipitation can be represented in a polymer/solvent/non-solvent phase diagram (Fig. 5). In this diagram, the initial polymer solution is situated in the stable region outside the binodal. After 'binodal demixing', indicated by pathway A, which is the most common phase separation mechanism, polymer solutions arrive in the metastable region between the binodal and the spinodal. In this region, polymer solutions will 'phase-separate' into a polymer-lean and a polymer-rich phase, indicated on the phase diagram by the A′ and A″ tieline ends respectively. Phase-separation takes place according to the 'nucleation and growth' mechanism, in which the formed nuclei grow and most often progress towards a phase-coalescence. 'Spinodal decomposition', the second and less frequent mechanism is represented by pathway B. This occurs whenever the polymer solution directly moves to the thermodynamically unstable zone within the spinodal. Again, two different phases are formed, but instead of developing well-defined nuclei, two co-continuous phases will be formed.[2,31]

However, not only the thermodynamic but also the kinetic aspects of the phase inversion process should be considered, more specifically the moment at which the developing membrane structure gets solidified. Fig. 6 shows the composition path of a cast polymer film (1: top of film, 2: middle, 3: bottom) in a phase diagram at a specific moment *t*, almost immediately after immersion. As more and more solvent will be exchanged by non-solvent, another decomposition path will exist for each subsequent moment. On the left-hand side (Fig. 6a), the binodal is crossed already at time *t* and demixing will start directly ('instantaneous demixing'). Under these conditions, a fine porous membrane structure will develop. On the right-hand side (Fig. 6b) however, at time *t*, all positions in the film

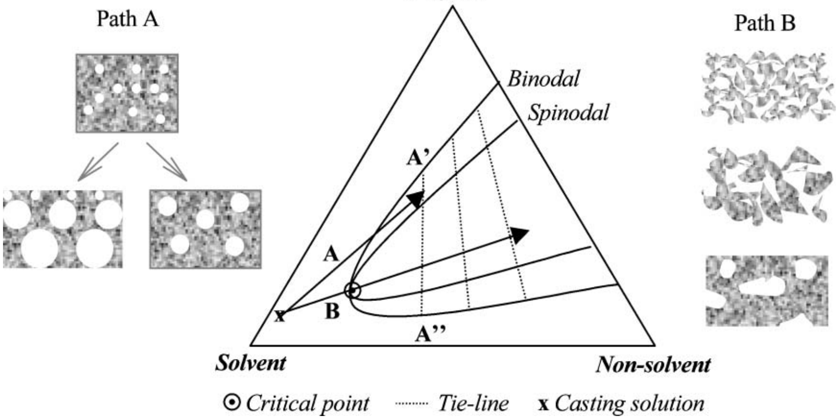


Fig. 5 Schematic representation of the mechanism of phase separation during membrane formation (taken from ref. 31).

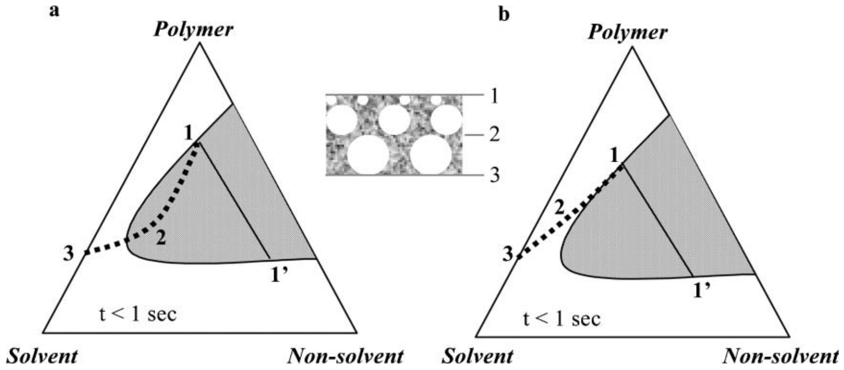


Fig. 6 Composition paths of two phase separation processes almost immediately after immersion: (a) instantaneous demixing, (b) delayed demixing (taken from ref. 31).

are still situated within the thermodynamically stable region. In this case, demixing will only start after some time when more non-solvent has diffused into the polymer film in such a way that the binodal can be crossed ('delayed demixing').[2,31]

A phenomenon often associated with immersion-precipitation, mostly with instantaneous precipitation, is the formation of macrovoids. These are elongated, finger- or tear-like pores that can extend over the entire membrane thickness, as shown in Fig. 4. They are generally considered undesirable as they cause mechanically weak spots in the membrane and thus severely limit the compaction resistance. Conditions favoring delayed demixing however can reduce or even suppress macrovoid formation, *e.g.* by selecting a non-solvent with limited miscibility with the solvent in the casting solution, by increasing the polymer concentration in the casting solution or by introducing an evaporation step before immersion of the cast film into the coagulation bath.[31,43–45]

A wide variety of experimental parameters have been shown to have an impact on the final morphology of asymmetric membranes, and consequently on their performance.[2,31,46] Combinatorial optimization techniques proved to be excellent tools to optimize such broad parameter spaces, as exemplified for a PI-based SRNF-membranes where the membrane with optimized composition showed considerably higher fluxes and rejections than commercial MPF-50 and Starmem™ 120 (see below) membranes [DE-S].[30]

3.3.2 Polymer type. Many chemically stable polymer types have been used to prepare solvent stable, asymmetric membranes *via* immersion-precipitation[24,31,47] (Table 1). In this context of SRNF, a distinction should be made between asymmetric membranes, that are useful as such for separations in the NF-domain, and membranes (generally UF), that are not selective by themselves but might be useful as supports for composite NF-membranes. This distinction, clarified already in Fig. 2, is indicated in Table 1 by means of 'A' (asymmetric NF/RO-membrane) and 'S' (support). As can be seen, several polymers have been applied for both membrane types.

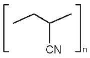
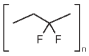
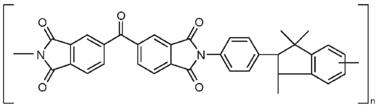
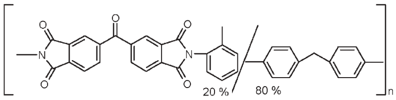
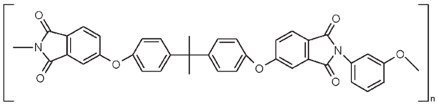
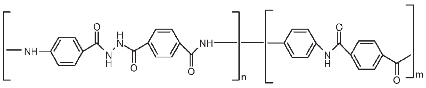
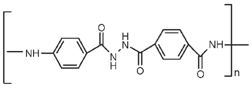
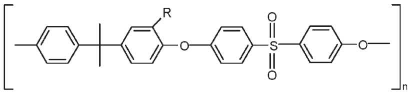
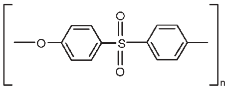
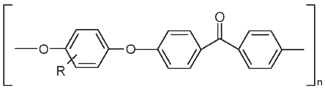
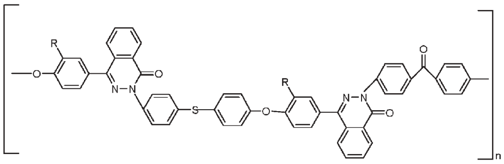
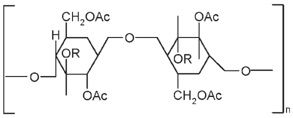
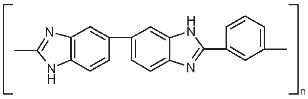
In both cases, solvent resistance should obviously be guaranteed. In order to be applicable in a broad range of solvents, the intrinsic chemical stability of the membrane-forming polymer itself is obviously crucial. This may however not pose limits on the processibility of the polymer nor on the pore structure and permselectivity of the membrane. Solvent stability is related to the chemical structure of the polymer and the presence of certain structural elements, like aromatic groups, imide bonds or F-atoms. Generally, co-polymerization induces rigid segments which impart solvent resistance.[24] Table 1 features intrinsically stable polymers, well suited for solvent filtrations as well as less stable polymers that are preferably used in aqueous environments but might be applicable in certain organic solvents as well or might be stabilized *via* cross-linking.

3.3.3 Composition of the casting solution. *Solvent.* Many polymers can be dissolved in polar aprotic solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA) or dimethyl sulfoxide (DMSO). The solvent choice is obviously restricted by the polymer type, but the mutual affinity between the solvent in the casting solution and the non-solvent in the coagulation bath is also of major importance for the membrane morphology. Several authors reported a higher flux through asymmetric membranes prepared from DMF-containing casting solutions compared to NMP-containing solutions when using water as immersion medium.[48,49]

Polymer concentration. By increasing the initial polymer concentration in the casting solution, a more concentrated zone is obtained in the polymer film at the polymer/(non-solvent)-interface. Hence, non-solvent in-diffusion is slowed down and demixing delayed, resulting in membranes with thicker and denser skin-layers and sublayers with lower porosities.[2,31] This obviously results in higher selectivities but lower permeabilities.[23,50–54] Higher casting solution viscosities, as in the case of more concentrated polymer solutions, are also known to suppress macrovoid formation in the substructure of asymmetric SRNF-membranes.[50]

Additives. Addition of a third component to the casting solution consisting of a polymer and a solvent, is a widely used method to enhance the flexibility of the phase-inversion process. Co-solvent and non-solvent additives as well as polymers, inorganic salts and surfactants have been commonly used.[31] This creates a highly complex thermodynamic/kinetic situation that is hard to rationalize and surely to predict. The

Table 1 Polymers used to prepare solvent stable, integrally skinned asymmetric membranes *via* phase inversion, applicable as such (A) or as support (S)

Polyme	Abbreviation	Molecular structure	Membrane type	References
Polyacrylonitrile	PAN		A S	85,87,88 6–8,16,20,24,27,35,39, 53,83,84, 86,87,98, 109,110,113–115, 117–124,129–131,136, 138,226,227,255,300
Poly(vinylidene fluoride)	PVDF		S	36,81,104,109,112,236
Polyimide (Matrimid®)	PI		A S	32,33,80,284–286,303 12,24
Polyimide (Lenzing P84)	PI		A S	23,80,223,303 67,82
Poly(etherimide)	PEI		A	52,57,109,299
Polyamide	PA		A	61,77
Poly(amide hydrazide)	PAH		A	60
Polysulfone (R = H)	PSf		S	30,51,63–65,109,236
Poly(ethersulfone)	PES		A S	50 34, 66
Poly(ether ether ketone) (R = H) Sulfonated PEEK (R = SO_3H)	PEEK SPEEK		A	69
Poly(phthalazinone ether sulfone ketone) (R = H), Sulfonated PPESK (R = SO_3H)	PPESK SPPESK		A (S)	54, 56
Cellulose acetate	CA		A	62, 74
Polybenzimidazole	PBI		S	40

most important ones with respect to SRNF-membrane formation – volatile solvents, non-solvents and pore-forming additives – will be discussed below.

Volatile solvents. The addition of volatile co-solvents (*e.g.* tetrahydrofuran (THF) or 1,4-dioxane) to casting solutions offers an easy way to enhance selectivities of asymmetric membranes. By allowing partial evaporation of the volatile solvent between the casting and immersion step, a skin-layer with elevated polymer concentration can be formed. This densified skin-layer acts as a resistive barrier between the coagulation bath and the interior region of the film, slowing down the diffusion of solvent and non-solvent. Due to this mass transfer resistance, the sublayer underneath shows slower demixing and precipitation kinetics, hence less macrovoids will be developed. Casting membranes from polymer solutions with an optimal (co-solvent)/solvent-ratio thus allows asymmetric membranes to be formed, consisting of a defect-free, ultrathin and dense skin-layer on top of a highly porous sublayer with sponge-like structure.[29] This technique, originally applied to synthesize selective GS-membranes,[46,51,55] was used to prepare highly selective asymmetric SRNF-membranes made from PI,[23,32] poly(ether imide) PEI[52] and sulfonated poly(phthalazine ether sulfone ketone) (SPPESK).[54]

Non-solvent additives. The addition of non-solvent additives to polymer solutions can greatly improve the performance and structure of asymmetric membranes. In GS, these additives are known to enhance the permeability and/or selectivity due to the formation of defect-free skin-layers and sublayers devoid of macrovoids.[46,55] Non-solvent additives have also been used to control the porosity of asymmetric NF-membranes.[32,54,56,57] Their effect on membrane structure and performance is highly dependent on the non-solvent power of the additive, its concentration in the casting solution and on the specific polymer/solvent system. When evaporation is part of the membrane formation process, the volatility of the non-solvent should also be taken into account.[58]

In the synthesis of PPESK-based NF-membranes from NMP-solutions, addition of ethylene glycol methyl ether (EGME) resulted in a sponge-like membrane morphology, as attributed to the destabilizing influence of the additive on the casting solution. The resulting flux decrease and rejection increase were less pronounced when adding the less polar butanone.[54] In a related study, PPESK-based NF-membranes were prepared by simultaneously adding the weak non-solvent additive EGME, forming a sharp interface between the coagulant and the PPESK/NMP casting solution, ánd the strong non-solvent additive acetic acid, bringing the polymer solution close to the binodal composition.[56] A similar approach allowed the preparation of PEI-based membranes by simultaneously adding diethylene glycol dimethyl ether (DEGDME) and acetic acid.[57] Bulut *et al.* described the combinatorial synthesis and optimization of high-performing PI-based SRNF-membranes by adding water, acetone, *i*-propanol and *n*-hexanol as non-solvent additives.[32]

Non-solvent additives can both suppress or induce macrovoid formation, depending on their content in the casting solution. Adding non-solvents in small concentrations induces macrovoid formation, while beyond a certain concentration limit, a large number of stable polymer-lean nuclei is induced, which hinders further growth of nuclei and formation of macrovoids.[59] The latter effect is reinforced by the lowered osmotic pressure difference near the non-solvent moving front upon immersing the polymer film.[43]

Pore-forming additives. Addition of inorganic salts, such as LiCl and $LiNO_3$, to casting solutions for poly(amide hydrazide) (PAH) membranes induced higher water permeabilities without lowering salt rejections. The Li salts are mainly concentrated at the air/film interface during the evaporation step, and subsequently extracted by the non-solvent upon immersion.[60] Furthermore, the addition of Li salts enhances the polymer solubility and allows control over the viscosity of the casting solution and the evaporation rate after casting.[61] $Mg(ClO_4)_2$ has been added to increase the porosity of cellulose acetate (CA) asymmetric membranes. Upon immersion in the non-solvent, water molecules aggregate around the Mg^{2+} cations, resulting in membranes with increased permeability but reduced selectivity.[62]

Alternatively, organic pore-formers can be applied. Polymers, such as PEG and polyvinylpyrrolidone (PVP) have been used to increase the porosity of asymmetric PSf,[63–65] PES,[66] PI[67] and PAN[68] membranes. Besides the concentration of these additives in the casting solution, their MW also determines the structure of the ultimate membrane. A higher concentration of PEG for example results in more porous membranes due to a lower thermodynamic stability and a higher non-solvent (water) inflow into the cast film upon immersion.[65] Sulfonated poly(ether ether ketone) (SPEEK), another highly hydrophilic polymeric additive, has a similar effect on water ingression when added to PSf/NMP casting solutions, thus resulting in increased porosities and water permeabilities. Furthermore, PSf/SPEEK blend membranes bear a surface charge, explaining the higher rejections for charged molecules.[69] A mixture of high MW (PVP, PEG, *etc.*) and pore-forming additives (mono- or polyfunctional alcohols) was claimed to be crucial for the synthesis of asymmetric PBI hollow fiber membranes, that can be used as such or as coatable supports for composite membranes. After cross-linking with alkyl halides at elevated temperatures, these membranes were shown to be stable in organic solvents, including NMP.[40] Aromatic pore-formers, *e.g.* pyrene, phenanthrene and PS, allowed the synthesis of PI-based SRNF-membranes with MWCOs in the range 400–650 Da in toluene.[70]

Addition of surfactants to a poly(methyl methacrylate)/acetone casting solution was shown to induce or suppress macrovoids, depending on the miscibility between the added surfactant and the coagulant.[71]

3.3.4 Evaporation. Similar to the addition of a volatile solvent, increasing the evaporation time prior to immersion enlarges the region with elevated polymer concentration. A top-layer is thus formed with higher resistance towards mass transfer between the coagulating non-solvent and the remaining solvent in the polymer film, causing a delayed onset of demixing.[31,51,55] Evaporation can be achieved by forcing a convective airflow over the cast film or by allowing the film to evaporate freely in the air. Several factors have to be considered: evaporation time and temperature, relative air humidity, and – when a convective flow is applied – air velocity. Increased evaporation times or higher temperatures induce lower permeabilities but higher selectivities as shown for PI,[23,72,73] PSf,[51] PEI,[52] polyamide (PA),[61] PAH,[60] CA[74] and PPESK.[75] Parallel with the rejection improvement, macrovoids tend to decrease, both in size and number, and ultimately vanish upon increasing the evaporation time.[74]

3.3.5 Coagulation medium. A strong mutual interaction between solvent and non-solvent, and thus an elevated exchange rate, enhances the demixing process, and favours the formation of membranes with a thin top-layer and a porous sublayer with macrovoids. A straightforward way to manipulate the solvent/non-solvent exchange rate and consequently also the membrane morphology is to change the composition of the coagulation bath.[2,31]

Several authors experimentally demonstrated that increased concentrations of (higher) alcohols in an aqueous coagulation bath, decreases the velocity of the diffusion front upon immersion, making macrovoids disappear.[48,50,76] A similar effect on membrane morphology was induced by adding the same solvent to the coagulation bath as the one used to dissolve the polymer, *i.c.* PA or PI.[77–79] A third way was by adding oligomeric or polymeric substances, *e.g.* octylphenoxypolyethoxyethanol, during PI-membrane preparation.[80]

Increased coagulation bath temperatures obviously enhance the solvent–non-solvent exchange rate, resulting in membranes with higher porosities and more macrovoids. However, a significant decrease of the water permeability through PES-membranes was observed upon increasing this temperature in the range 12–47 °C, while rejections slightly decreased.[50] For PAH-membranes on the other hand, increased coagulation bath temperatures promoted salt rejection.[60] Yeow *et al.* quenched a PVDF/DMA casting solution in an aqueous, $LiClO_4$-containing coagulation bath with progressively increasing temperature. In the presence of the additive, higher temperatures promoted the formation of an interconnected pore structure, resulting in higher permeation rates.[81]

3.3.6 Post-treatment. In order to increase the separation performance of asymmetric membranes and to increase their long-term stability, several post-treatment or conditioning procedures can be used, such as annealing (wet or dry), cross-linking, drying by solvent exchange and treatment with conditioning agents.[31] The crucial role of post-treatment has often been neglected, and is probably often part of the 'skills' not explicitly reported in literature. Frequently, a wrong post-treatment can turn the intrinsically best possible membrane into a very bad one. Moreover, correct post-synthesis conditioning also matters on the level of polymeric supports, especially in the case of solvent cast TFC membranes.[24]

Annealing. Using a thermal annealing procedure, asymmetric PI-based membranes with exceptional solvent resistance and high permeabilities have been obtained. The gradual heating first drove off residual solvent (100–200 °C), then caused cyclization (imidization) of the amic acid groups (200–250 °C) and finally cross-linking (>250 °C). The annealed PI membranes are useful as such for UF, or may be used as supports for TFC membranes applicable in SRNF.[82] Similarly, the rejection of PI-based SRNF-membranes could be considerably improved by heating for a short period (30 s) at high temperatures (260 °C), mostly at the expense of permeability.[80] A drastic flux decline was also observed upon heating (0–150 °C) an asymmetric PI (Lenzing P84) SRNF-membrane, while the MWCO remained largely unaltered. A gradual loss of the nanoporosity in the separating top-layer was noticed, as well as a significant shrinkage of the membrane structure, with the typical nodular structure being replaced with a continuous, non-porous layer interspersed with nodules.[23]

Cross-linking. In order to enhance chemical stability and rejection properties, asymmetric membranes can be subjected to chemical, plasma or photo-induced cross-linking. This is exemplified here for PAN-based asymmetric membranes, either used as such or as support. Membrane Products Kiryat Weitzman patented a synthesis procedure for TFC SRNF-membranes with a cross-linked PAN support.[27,83,84] Cross-linking was realized by immersing the PAN membranes in an organic or inorganic base, followed by heat treatment at elevated temperatures (110–130 °C). In addition to the improved chemical stability, membrane selectivity was enhanced considerably. According to another cross-linking procedure, microporous PAN membranes could be transformed into asymmetric cationic NF-membranes by taking advantage of the surface tension forces within the capillary pores upon heat treatment in the presence of $ZnCl_2$. This way, the pores in the UF-membrane could be easily reduced to pores that allow NF. Pore surface functional groups were subsequently introduced by hydrolysis of the nitrile groups with NaOH.[85] Hicke *et al.* prepared poly(acrylonitrile-*co*-glycidylmethacrylate) membranes by conventional immersion-precipitation, followed by a post-treatment with ammonia as a bi- or trifunctional cross-linking agent. This ammonolysis resulted in an extensive cross-linking, yielding highly solvent resistant UF-membranes, applicable in DMF as well as in strongly acidic and alkaline media.[53,86] GKSS researchers claimed a procedure for the synthesis of PAN-based membranes, useful for UF and NF. The method is based on the use of a co-monomer with a reactive group (*e.g.* epoxy, alkoxysilyl groups) that can react with a cross-linking agent (*e.g.* amines).[87] According to another cross-linking procedure, PAN-based SRNF-membranes can be made by Ar low-temperature plasma-treatment of UF-membranes and subsequent styrene grafting in the vapor phase. The hydrophobized plasma-grafted membrane was shown to be useful to recover dewaxing solvents, typically toluene and methyl ethyl ketone (MEK), from lube oil.[88]

Drying by solvent exchange. In order to maintain or even enhance pore and surface structure, asymmetric polymeric membranes are preferably dried by a multiphase solvent exchange. Hereby, the residual non-solvent present in the membrane after immersion is replaced by a first solvent, which is miscible with the non-solvent. This solvent is then replaced by a second, more volatile solvent, which can be removed easily by evaporation to obtain a dry membrane. This solvent exchange procedure minimizes the risk on pore collapse upon drying.[29] According to this procedure, asymmetric PI membranes can be post-treated with low MW alcohols or ketones, and subsequently with hexane or toluene.[80] The performance, flexibility and handling of asymmetric membranes can be further improved by impregnating them with conditioning agents such as lube oils, glycerol or long chain hydrocarbons. Addition of lube oil to a second solvent exchange bath containing MEK and toluene, was claimed to considerably enhance the toluene flux through PI-based SRNF-membranes.[80]

3.4 Interfacial polymerization

3.4.1 Introduction. Interfacial polymerization has become a well-established and useful technique to prepare the dense, active top-layer of composite RO- and NF-membranes. The general focus has been on the development of membranes for aqueous applications, mainly sea water desalination, but the membranes might be useful for filtrations in certain organic solvents as well. Pioneering work on interfacial polymerization has been performed by Cadotte.[30,89] The technique entails the application of an ultra-thin film upon an asymmetric, porous support-layer *via* an *in-situ* polymerization reaction occurring at the interface between two immiscible solvents containing reactive monomers (Fig. 7). After impregnating an UF-membrane, typically in an aqueous diamine solution, and removing the excess water, the saturated support is contacted with an organic phase containing acyl halides. Both monomers then react with each other and quickly form a thin selective PA layer, from several tens of nm to several μm thick, that remains attached to the substrate. As soon as the top-layer is formed, it acts as a barrier for further monomer transport thus controlling the top-layer thickness.[30,31,43] A large number of TFC membranes have thus been successfully developed mainly consisting of a PA top-layer, but poly(amide imide) (PAI), poly(ether amide) (PEA), polyurea and poly(urea amide) (PUA) have been mentioned too.[30]

The composition, morphology and performance of interfacially polymerized membranes depends on several parameters, including the concentration of the reactants as well as their partition coefficients and reactivities, possible additives, solubility of the nascent polymer in the solvent phase, overall kinetics and diffusion rates of the reactants, presence of by-products, competitive side reactions, cross-linking reactions and post-reaction treatment.[30]

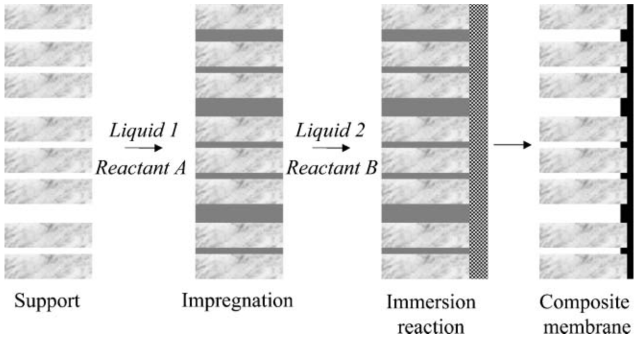


Fig. 7 Schematic illustration of the interfacial polymerization method (taken from ref. 31).

3.4.2 Supports. Supports for interfacial polymerization have to meet different requirements, as already stated above. The support-layer plays a crucial role as it serves as a reservoir for one of the precursors, and co-defines the interface where the reaction will take place. The usefulness of interfacially polymerized TFC membranes for non-aqueous filtrations partly depends on the solvent resistance of the support-layer. Due to its high durability, resistance to pH variations and to a wide range of solvents, polypropylene is a particularly interesting supporting material to obtain solvent resistant TFC membranes.[38] However, due to the hydrophobicity of the polymer, a hydrophilization of the support is essential to ensure appropriate wettability and adhesion between top-layer and support. This has been realized *via* low temperature plasma polymerization with hydrophilic monomers like allylamine[37] or surface oxidation with chromic acid.[38] Interfacial polymerization on top of a PAN support containing carboxylic acid groups at its surface was shown to induce ionic bonds between the formed PA top-layer and the support. Due to the interaction of amines with these carboxylic groups, formed *via* base-induced partial hydrolysis of the nitrile groups in the PAN support, a considerable increase of the water flux through these TFC membranes was noticed, as well as a slight increase of the salt rejection. In addition to an improved performance, the introduction of ionic bonds also proved beneficial for the membrane chemical stability.[35]

3.4.3 Monomers. Most interfacially polymerized TFC membranes typically show a trade-off between permeability and solute rejection, which can partly be overcome by carefully selecting monomers and polymerization conditions.[30,90,91]

Amines. In general, aromatic diamines show better rejections, but lower fluxes compared to aliphatic diamines. Hence, the former are typically used for RO-membranes, while piperazine or amine-substituted piperidines are preferred for NF-applications.[30] One of the main factors affecting rejection is the position of the amine and acyl chloride groups on the aromatic rings, as been shown for the reaction of *o*-, *m*- and *p*-phenylene diamine (*o*-, *m*- and *p*-PDA) with isophthaloyl or terephthaloyl chloride (IPC or TPC).[90,91] The most performant PA-membrane, commercialized as FT-30, was obtained by polymerizing *m*-PDA and trimesoylchloride (TMC).[30] Due to the triple functionality of the acyl compound, highly cross-linked, mechanically stable and selective network structures were formed. The unreacted acyl groups can also be hydrolysed, leading to TFC membranes with fixed charges. This hydrophilization enhances water fluxes, while decreasing the density and rejection of the top-layer.[90,91]

Various water phase additives can increase the performance of PA membranes. The use of polymeric amines, like poly(aminostyrene), in combination with TMC resulted in higher water fluxes but lower rejections. Addition of small amounts of *m*-PDA to the aqueous amine phase significantly enhanced rejection rates without affecting water fluxes.[90,91] Alternatively, addition of 3,5-diamino benzoic acid to the water phase enhances water fluxes as it introduces non-polymerizable carboxylic groups in the PA film, thus increasing the hydrophilicity.[91] A similar hydrophilising and flux-enhancing effect has been obtained by adding *m*-phenylenediamine-5-sulfonic acid (S-*m*-PDA).[92] In order to increase the chlorine resistance of PA-based TFC membranes, ester linkages have been incorporated thus forming poly(ester amide) membranes. This was realized by adding *e.g.* *m*-aminophenol, bisphenol-1 or hydroquinone to an aqueous phase containing *m*-PDA.[93] In order to prepare loose RO- or NF-membranes, *m*-PDA is often blended with piperazine. In addition to its improved chlorine resistance, this aliphatic diamine also provides higher free volumes and larger pore sizes to the active layer.[94]

The wettability of the – often relatively hydrophobic – support can be enhanced by adding wetting agents (*e.g.* PEGs) to the aqueous diamine solution.[94] Overall membrane performance can be enhanced by adding swelling agents (*e.g.* DMF), improving the interaction between the top-layer being formed and the swollen support.[94] Aqueous phase additives, *e.g.* lower alcohols (*e.g.* *i*-propanol or *n*-propanol), can enhance the contact between both reagent phases. They tend to make the interface between both phases more diffuse, and consequently have a beneficial effect on film formation, thus leading to more selective membranes.[95] However, when the interface gets too diffuse, the path length of the monomers to the reaction site can become excessive, making film formation difficult. This results in rather rough membrane surfaces often showing defects. Nevertheless, a limited surface roughness is beneficial for the permeability.[96] Similarly, phase transfer catalysts (PTCs) are known to enlarge the contact surface between the reacting phases, thus enhancing the polymerization rate.[95]

Acyl chlorides. Similar to amines, a broad range of aromatic acyl chlorides have been used to prepare PA-based TFC membranes. The number and position of the acyl halide groups on the aromatic ring is a major factor affecting the salt rejection, as they determine the chain structure and the cross-linking degree of the formed PA network.[91] The hydrolysis of acyl chloride groups to carboxylic acid groups has an important effect on the hydrophilicity, surface charge and degree of cross-linking of the ultimate membrane, as already stated above.[90] In addition to acyl chloride monomers, polymers with acyl chloride pendant groups can be used. Mixtures of IPC with poly(isobutylmethacrylate–*co*-acryloyl chloride) in combination with a tetrafunctional aromatic amine showed good film forming properties.[97] The contact between the phases containing the reactive monomers can be improved by (partly) replacing the organic phase, generally hexane, with benzene or 1,2-dichloroethane being better solvents for the formed PA polymer. This way, rejections could be significantly improved.[95]

3.4.4 Polymerization parameters. Higher monomer concentrations,[94,98,99] higher reaction rates[90] and longer polymerization times[94,99,100] generally improve the efficiency of film formation. This results in thicker and denser barrier-layers with increased rejections but decreased fluxes. The polymerization reaction takes place at the interface between both phases, but the nascent film then gradually grows away from the aqueous phase as the amines diffuse through the interface and the film being formed. As the reaction continues, the film thickness will prevent further amine diffusion and stop film growth.[94] Progress on modeling the kinetics of film growth has been achieved recently, and improved predictions of membrane properties (surface morphology, charge, MW distribution, *etc.*) can now be made, despite difficulties of fast reaction rate and non-steady-state characteristics of the interfacial polymerization process.[100]

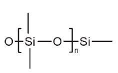
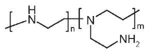
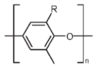
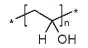
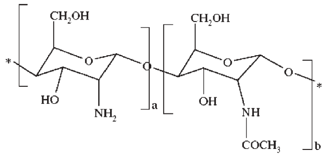
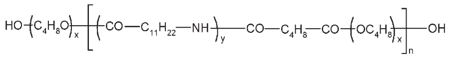
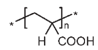
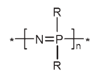
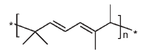
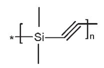
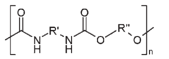
3.4.5 Post-treatment. The performance of TFC membranes can be further enhanced by applying an adequate post-polymerization treatment. Different techniques have been described including grafting, curing, plasma, UV and chemical treatment. A treatment of the active PA layer with ammonia or certain alkylamines at elevated temperatures has been claimed to be flux-enhancing, without altering rejection.[101] Alternatively, NF-membranes have been obtained by contacting the PA layer of RO-membranes with strong mineral acids (*e.g.* phosphoric acid), followed by treatment with a rejection enhancing agent (*e.g.* tannic acid).[102]

3.4.6 Non-aqueous applications. Although PA-based TFC membranes have been specifically designed to separate aqueous feed streams down at a molecular level, they can be applied in certain organic solvents as well.[97,103,104] This obviously depends on the specific molecular structure of the top-layer and the stability of the support-layer. TFC membranes synthesized from PIP/*m*-MPD and TMC performed well in methanol, ethanol and acetone, less in *i*-propanol and MEK, and gave no flux at all in hexane.[105] These membranes are thus clearly not suited for filtrations in more apolar media. In order to allow hexane-based applications, non-reactive polydimethylsiloxane (PDMS) can be added during the polymerization reaction. The resulting silicone-blended PA membrane showed high hexane permeabilities. The hydrophilicity change obtained upon blending can thus broaden the scope of PA membranes.[106,107] However, PA-based TFC membranes can also be applied as such for filtrations in the more apolar solvents. A method for the separation of lube oil from organic solvents (*e.g.* furfural, MEK/toluene, *etc.*) with a cross-linked PA membrane has been patented, using poly(ethylene imine) (PEI) and a diisocyanate on a solvent resistant nylon-6,6 support.[108] Alternative to PA, PAI has been reported to be useful for the synthesis of thermally and chemically stable TFC membranes.[34]

3.5 Solvent-casting

3.5.1 Introduction. A relatively simple membrane preparation technique, of particular interest for SRNF-membranes, is the coating of a polymer solution on a support. The coating solution can be cast on the support with a casting knife or spread over the tilted support by pouring, depending on its viscosity.[24,31] The latter mainly depends on the MW of the dissolved polymer, the solvent (mixture), the temperature and concentration of the solution, and possible additives. Increased viscosities not only enhance the thickness of the coated film,

Table 2 Polymers used to prepare TFC SRNF-membranes *via* solvent-casting

Polymer	Abbreviation	Molecular structure	Refs
Polydimethylsiloxane	PDMS		6–8,12,16,20,24, 26,39,106, 107,109–121,226,227,241, 255,270, 275,284,285,299
Poly(ethylene imine)	PEi		83,84,108,122,123,126,313
Poly(2,6-dimethyl-1,4-phenylene oxide) (R = H)	PPO		124,125
Sulfonated PPO (R = SO_3H)	SPPO		
Bromomethylated PPO (R = Br)	PPO-Br		
Poly(vinyl alcohol)	PVA		126–128
Chitosan			129–131
Poly(ether-*b*-amide)	PEBAX		86,244
Polyacrylic acid	PAA		132–134
Polyphosphazene	PPz		135
Poly(aliphatic terpene)			136
Poly-[1-(trimethylsilyl)-1-propyne]	PTMSP		137
Polyurethane	PU		138

but also prevent intrusion of the coating solution in the support. Such intrusion should be avoided as it can drastically lower fluxes. The parts of the top-layer present in the pores of the support indeed suffer from sterical restrictions and thus limit their swelling during filtration.[24] On the other hand, a limited intrusion in the layer might be beneficial for the adhesion of the top-layer. Multiple coatings obviously result in thicker top-layers and thus lower fluxes, but might be necessary to repair defects. Apart from its influence on the solution viscosity, the solvent in which the polymer is dissolved co-determines the adhesion between polymer solution and support. The support characteristics, particularly surface roughness, porosity and hydrophilicity, also influence the adhesion of the top-layer. Livingston and co-workers studied the influence of the support (PAN, PEI, PVDF and PPSf) resistance on the overall mass transfer coefficient of PDMS-based TFC membranes for aromatics extraction from aqueous streams.[109]

3.5.2 Polymers for composite SRNF-membranes. The polymer choice depends on many parameters including the mechanical strength and chemical stability of the polymer, its film forming properties, solubility in solvents, possibility to cross-link, *etc.* As solvent casting mostly leads to non-porous top-layers, affinity of the polymer for the solvent to be permeated is a crucial aspect. PDMS, PEI, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(vinyl alcohol) (PVA), chitosan and other cellulose derivatives, poly(ether-*b*-amide) (PEBAX), polyacrylic acid (PAA), polyphosphazene (PPz), poly(aliphatic terpenes), poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and polyurethanes (PUs) have all been studied as coating materials (Table 2). Before or after drying, a possible cross-linking step can give the coated barrier-layer more stability and possibly also better separation properties. In general, more cross-linked membranes, especially those with an elastomeric coating, are denser, less permeable and more selective. The type and concentration of the cross-linker, the reaction time, temperature and possibly pH all determine the degree of cross-linking.

PDMS. PDMS is the most important elastomeric member of the organosiloxanes, usually known as 'silicones'. It contains a siloxane (Si–O) backbone substituted with methyl groups. PDMS is chemically stable in all organic solvents when cross-linked, but it is preferably used in apolar solvents, due to its low polarity. Prior to coating a PDMS solution, the support is often water-impregnated to prevent extensive intrusion, and sometimes pretreated with an adhesion promoter. After evaporation of the solvent, cross-linking can be completed at elevated temperatures.[110]

PDMS already showed great utility as membrane material in industrial processes with organic solvents. A PDMS/PI membrane was used in a pressure driven process to separate PEGs from ethanol.[111] Schmidt *et al.* developed PDMS/PVDF composite membranes, post-treated with electron irradiation, and used them to separate corn seed oil and PEG from toluene and ethanol respectively.[112] In a Texaco-patent, a PDMS/PAN composite membrane is described, prepared from a disilanol-terminated siloxane, cross-linked with toluene diisocyanate, and tested in the separation of dewaxed oil from MEK/toluene mixtures.[113] Membrane Products Kyriat Weitzman (a later Koch acquisition) developed a PDMS/PAN membrane, belonging to the SelRo® membrane series of Koch Membrane Systems. Prior to application of the silicone coating, the support was treated with silanol-terminated polysiloxane as 'pore protector' to prevent the pores from collapsing upon curing the silicone layer and to prevent intrusion.[26]

Despite its broad chemical stability and its frequent use in SRNF applications, the extensive swelling of PDMS in organic solvents, is an important issue which limits its utility in some apolar solvents. This promotes the less selective convective transport over the slower diffusive transport[110,114,115] and might induce top-layer peel-off. Several solutions have been proposed in literature to overcome this swelling problem, *e.g.* the use of halogen-substituted silicone rubbers containing 1,1,1-trifluoropropyl groups.[116] Alternatively, extra cross-linking of silicone rubbers has been realized *via* plasma treatment.[117] Both approaches however significant lowered fluxes. This was not the case when introducing the extra cross-linking *via* incorporation of porous fillers with the right surface properties to interact well with the polymer matrix, hence reducing swelling and rendering the top-layer mechanically and chemically more stable.[118] Zeolites are such fillers of which additionally the appropriate pore structure can be selected so as to exclude the solute to be retained but let the solvent permeate. Such enhanced rejection combined with increased permeability was realized by incorporating a silicalite zeolite in PDMS.[24,110,119,120] Incorporation of other zeolites did not lead to similar results: ZSM-5 interacted too strongly with most solvents, hence slowing down solvent transport,[110] and the wider pore structure of USY adsorbed too many polymer chains inside, leaving no space for solvent molecules to pass.[120] These zeolite-filled membranes allowed separations in apolar solvents and at increased temperatures.[110,120] A top-layer thickness of 4 μm could be realized by selecting the right set-up and parameters for the coating procedure, *i.e.* coating angle, polymer and filler concentration. With such thin and highly permeable barrier-layers, support characteristics, such as surface roughness and porosity, were shown to influence the performance of the composite membrane. As mentioned above, the preservation of the pore structure of the support was crucial while curing the PDMS top-layer after dip-coating. An optimized support treatment, mostly overlooked in literature, involving solvent exchange and impregnation with non-volatile solvents, increased the permeability of the composite membranes by an order of magnitude.[24]

Swelling was suggested to be the main reason – together with solute clustering – for the low rejection of PEGs in ethanol, alkanes and toluene for a laboratory-prepared PDMS/PAN membrane.[7,39] A linear relation between solvent permeability and the ratio membrane swelling/solvent viscosity was observed for the transport of solvents through PDMS or a more hydrophilic poly(ethylene oxide) (PEO)-PDMS-PEO tri-block copolymer.[16]

Related to this swelling is the aspect of compaction. It is reasonable to assume that for rigid polymers in non-swelling conditions, compaction at filtration pressures should be negligible. This seems however much less straightforward for elastomers, like PDMS, in a swollen state. Swelling experiments on a PDMS slab pointed out that, due to the applied pressure, the top-layer is 'squeezed out' slowly till equilibrium. This solvent squeezing from the membrane proved to be reversible.[20,121]

PEI. Several patents describe the synthesis of membranes with a chemical bond between the PEI top-layer and the support. PAN membranes can be treated with compounds bearing diazonium functionalities that react with the support, and a multifunctional bridging molecule (*e.g.* cyanuric chloride), which is a successful cross-linker for PEI.[83,84,122] According to this procedure, highly stable PEI/PAN composite membranes could be prepared showing high permeances for DMF, MEK and DCM and almost complete rejection of congo red (697 Da) [CU-S].[123]

PPO. Kyriat Weitzman patents mention the development of PPO-derived composite membranes for applications in organic solvents. More specifically, solutions of bromomethylated PPO (PPO-Br) and an amine cross-linking agent were used to coat insolubilized PAN or PP supports. When immersed in various organic solvents, membrane swelling to an extent of no more than 10% was noticed. Depending on the specific cross-linker used, rejections up to 99% for Sudan IV (380 Da) in EA could be reached [CU-S].[125] Sulfonated PPO (SPPO) was rendered insoluble in ethanol and *i*-propanol by ion-exchange of the protons with sodium.[125]

PVA. Fluxes and MWCO values of PVA, a very hydrophilic and relatively stable polymer, sharply decrease after heat treatment above 80 °C due to enhanced crystallization of the polymer. Chemical cross-linking can reduce crystallinity, and thus increase permeability. PP supports were coated with a solution of PVA and azo dyes. These ionic, reactive dyes containing a dichlorotriazinyl group, react with the hydroxyl groups of PVA, while their ionic groups resulted in composite membranes with fixed charge. Furthermore, PVA coatings have been treated with cyanuric chloride and $NaHCO_3$, after which a PEi coating has been applied to increase the degree of cross-linking and selectivity.[126] Jegal *et al.* added glutaraldehyde as a cross-linking agent to PVA solutions, while sodium alginate was used as ionic polymer.[127] Surface cross-linking is another route, where dry PVA films are contacted with a cross-linker solution containing most often malic acid.[128]

Chitosan and cellulose ethers. Chitosan, an analogue of CA, most often partly acylated, needs cross-linking, *e.g.* with glutaraldehyde after treatment with aqueous alkali. Kumar and Musale reported on the swelling of a cross-linked chitosan/PAN membrane showing solvent resistance in alcohols, ketones, esters and aliphatic hydrocarbons.[129,130] The permeability in lower alcohols, MEK and EA was stable, while the hexane flux was negligible.[131] Peinemann and co-workers reported the synthesis of composite SRNF-membranes, comprising a top-layer of cellulose ethers, *e.g.* hydroxymethylcellulose, coated on a porous cross-linked PAI support, showing oil rejections up to 99% in acetone. A PEBAX/PAN composite membrane turned out to be considerably less selective for the removal of oil from hexane [DE-S].[86]

Polyacrylic acid. PAA has mostly been cross-linked with ethylene glycol (EG).[132,133] In most cases, $Al(NO_3)_3$ has been added, which exerts an electric charge on the carboxyl group but also increases the cross-linking degree by the formation of complexes with the carboxyl groups.[134] To improve the membrane stability, the dried PAA/EG/Al layer can be further treated with toluene-2,4-diisocyanate, followed by a thermal treatment.[134]

PPz. Boye *et al.* patented the synthesis of composite NF-membranes comprising a porous inorganic support on which a nanoporous elastomeric PPz coating was deposited *via* solvent casting. The inorganic moiety imparted a better mechanical, thermal and chemical resistance to the composite membranes.[135]

Poly(aliphatic terpenes). Membranes with good stability in organic solvents were made on a PAN support on which an adduct of poly(aliphatic terpenes) and maleic acid was coated. Thermal cross-linking at 125 °C finalised the membrane, which was tested in the separation of dewaxed oil from MEK–toluene mixtures.[136]

PTMSP. PTMSP, a hydrophobic glassy polymer with extremely high free-volume, was coated on a commercial cellophane film, showed higher ethanol permeabilities than two silicone-based, commercially available SRNF-membranes, while rejection was highly dependent on solute charge.[137]

PUs. Novel PU-based composite membranes have been recently reported. A method was developed for the polymerization, casting, and crosslinking of a thin PU-film on a support membrane without pore penetration and with good adhesion to the support. A thin defect-free PU barrier-layer ($\sim$2.5 μm) was obtained by casting a reaction solution, containing a polyether polyol and a polyisocyanate precursor, a polymerization catalyst, a chain extender and a cross-linker on a porous, solvent-stable PAN UF-support. Rejections between 75 and 90% for the dye 4′,5′-dinitrofluoroscein (422 Da) in ethanol, EA, DCM and THF were shown, combined with high permeabilities [CU-S]. The structure of the PU network structure is highly flexible and can be controlled to a large extent by both chemical and physical cross-linking. In particular, the extent of swelling can be modulated by varying the composition of the reaction mixture, in such a way that the membranes can be tailored very precisely according to the requirements of specific solvents.[138]

3.6 Ceramic membranes

3.6.1 General preparation method. Ceramic membranes normally have an asymmetric structure composed of at least two – but mostly many more – different porosity levels to gradually decrease the roughness of the supporting layer and allow application of layers with gradually decreasing pore sizes. The most common ceramic membranes are made of Al, Si, Ti or Zr oxides, or of their mixed oxides.[2,29,31] The active top-layers of ceramic membranes are normally prepared *via* the sol–gel synthesis method, the successive steps of which are schematically shown in Fig. 8. Sol–gel synthesis is a very general method to convert a colloidal or polymeric solution of inorganic precursors into a gelatinous substance. It involves the hydrolysis and condensation reactions of alkoxides or salts

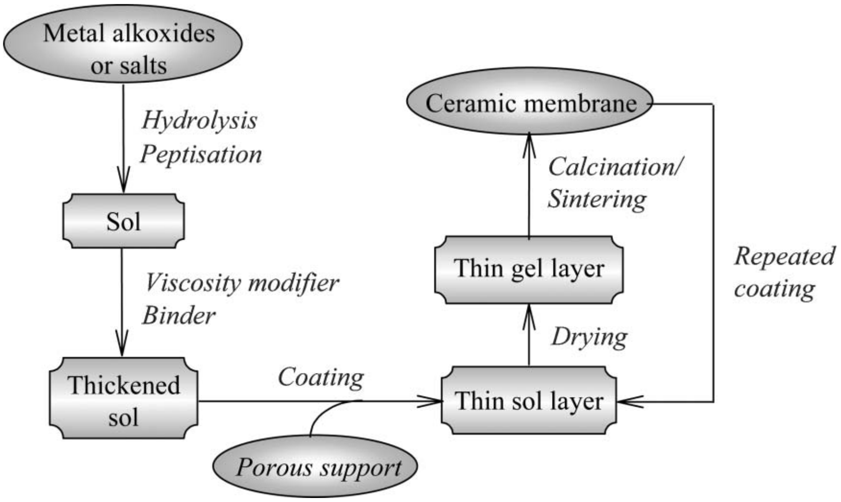


Fig. 8 Flow diagram for the preparation of microporous or mesoporous membranes *via* sol–gel techniques (taken from ref 31).

dissolved in water or organic solvents. Viscosity modifiers or binders are frequently added to the sol prior to layered deposition on a porous support *via* dip- or spin-coating. This is followed by gelation of the layer upon drying. A controlled calcination and/or sintering finally leads to the actual ceramic membrane.[31]

The sol is basically a stable dispersion of nanometer-sized particles, which allows an intimate mixing at molecular level of different precursors, and is thus capable of yielding homogeneous multicomponent ceramics. According to the structural nature of the sol which is tailored by controlled hydrolysis and condensation reactions, two major routes can be distinguished. In the 'colloidal gel' route, a metal salt or hydrated oxide is mixed with an excess of water. The hydrolysis rate is fast and a 'particulate' sol consisting of gelatinous hydroxide particles is formed. The primary colloidal particles are usually in the range of 5–15 nm. On the contrary, a much smaller amount of water is present in an organic solvent in the 'polymeric gel' route, in which the basic components are not really particles but rather polymeric molecules.[31] They have a mineral core surrounded by an organic shell which prevents aggregation.[139] Similar to the addition of less water, hydrolysis can be inhibited by adding chelating agents, such as acetylacetone.[140] In an alternative approach, the rate of hydrolysis can be further reduced by selecting precursors that hydrolyse slower, *e.g.* silica. The hydrolysis can be acid or base-catalysed.[139]

The interpenetration of the polymeric structures ultimately leads to the formation of the pores in the polymeric gel route.[141] In the colloidal gels, the final membrane pores are formed by the voids generated by the packing of the primary particles. The particle packing thus plays an important role here in affecting the resulting pore size of the final membrane. Micropores (diameter < 2 nm) can only be prepared from extremely fine colloidal sols, from polymeric sols and from inorganic–organic systems.[139] The fine colloids obtained through the colloidal sol route need to be stabilised (peptised), normally by an acid, to avoid aggregation of primary particles in the dispersion liquid.[142,143]

A sol layer is generally deposited on a porous support, possibly after ageing the sol for a certain period.[144] As the solvent in the sol evaporates upon drying, the concentration of particles can reach a threshold level, or the surface charges of the sol particles can change. This can lead to the transformation of the colloidal suspension into a semi-solid material with an interlinked network structure of particles or agglomerates, called a gel. Even though strictly not necessary for polymeric precursor sols,[145] a binder is often added to prevent crack formation in the subsequent process steps. PVA or cellulose derivatives have proven to be very effective here. As temperature is then increased, the primary particles grow and so do the membrane pores. The firing temperature is the ultimate control over the MWCO.[146]

3.6.2 Preparation of ceramic SRNF-membranes. Similar to polymeric membranes, the development of ceramic membranes for organic applications has its origin in fact in the preparation of membranes for treatment of aqueous streams, as reviewed recently.[140,147,148] The major challenge here was to turn the wide pores of the more common MF- or UF-membranes into nanometer-sized pores. In an attempt to make Zr- and Ti-based membranes for the NF-range, the particles in the sol-gel process were made smaller by optimizing precursor concentration, pH and temperature during hydrolysis. The limits of the system were found with particles of 2–3 nm diameter, leading to pores of 2–4 nm and MWCO-values of 1500–5000 Da. The attempts with SiO_2 were more successful leading to 1 nm pores.[147] For TiO_2 and ZrO_2, the same could only be realized when precursor hydrolysis took place in organic medium and with ligands (*e.g.* acetylacetone) added to sterically hinder the alcoholate hydrolysis.[140] TiO_2 membranes with a MWCO of 480 Da could be prepared, corresponding to 0.9 nm pores. Water permeabilities up to 20 l (m^2 h bar)$^{-1}$ were realized with a 50 nm thin top-layer having a porosity of 80% [CF-S].[145] This TiO_2-based NF-membrane has been commercialized as Inopor®[149] and has been applied since 2002 in treatment of textile waste waters.[150]

The problem of the intrinsic hydrophilicity of oxide pore surfaces prohibits permeation of alkanes or aromatics. The approach to cope with this problem by preparing mixed oxides was not successful.[151] Tsuru *et al.* thoroughly studied silica–zirconia membranes (Si/Zr molar ratio 9/1), first in aqueous feeds,[152] later in organics.[11,142] They prepared membranes with pore diameters between 1 and 4 nm by adjusting the colloidal diameter (from 11 to 16 nm) of the sol solution, corresponding to MWCO-values from 300 to more than 1000 Da. Their approach to optimize the membranes for non-aqueous applications consisted in hydrophobisation of the silanol groups in the pores *via* a gas-phase reaction with trimethylchlorosilane at 200 °C.[153] Ethanol fluxes of up to 3 kg (m^2 h)$^{-1}$ at 30 bar and 60 °C were obtained with a membrane containing pores of 1 nm diameter and a MWCO as low as 200 Da [CU-S].[154,155] Such silylation also allowed alkane fluxes through γ-alumina membranes.[156] The silylation of ceramic mesoporous membranes with silylating agents has been patented by HITK (Germany). With MWCOs down to 660 Da, exceptionally high toluene and methanol fluxes of 52 and 22 l (m^2 h bar)$^{-1}$ respectively are claimed [CU].[157]

3.7 Commercial SRNF-membranes

The current commercial market for SRNF-membranes is still very young and even though excellent membranes are available at present for some applications, they might be absolutely absent still for others. The limited number of commercially available membranes obviously hinders further industrial penetration of SRNF. Commercial SRNF-membranes include the Koch and Starmem™ membranes, the recently commercialized SolSep membranes, as well as the only ceramic HITK-T1 membrane. Apart from these membranes, especially designed for SRNF, membranes developed for the water treatment market, could be effective as well for SRNF in certain organic solvents.

3.7.1 Membranes specifically designed for SRNF. *Koch SelRO® membranes.* In the late nineties, Koch Membrane Systems[158] (USA) was the first company to enter the SRNF-market with three different membranes designed for solvent applications. The hydrophobic SelRO® MPF-60 membranes

(MWCO 400 Da, based on rejection of Sudan IV (384 Da) in acetone) has been taken off the market after a few years, and recently the other hydrophobic SelRO® membrane, MPF-50 (MWCO 700 Da, based on rejection of Sudan IV in EA) has been discontinued as well. Only the hydrophilic, MPF-44 membrane (MWCO 250 Da, based on rejection of glucose (180 Da) in water) is still available, in flat sheet as well as spiral-wound (MPS-44) module configuration. The membrane is claimed to be stable in aqueous mixtures of lower alcohols, hydrocarbons, chlorinated solvents (*e.g.* DCM, chloroform), aromatics (*e.g.* toluene, xylene), ketones (*e.g.* MEK), diethyl ether, EA, cyclohexane, propylene oxide, acetonitrile, THF and 1,4-dioxane. Koch also distributes an UF-membrane (nominal MWCO ~ 20000 Da), based on cross-linked PAN, available in both flat sheet (MPF-U20S) and spiral-wound (MPS-U20S) elements, claimed to be stable in all aforementioned solvents.[158]

With the SolSep and Starmem™ membranes not having been available freely for a long time, MPF-50 has been the most studied commercial SRNF-membrane. It is supposed to be a composite multi-layered membrane, consisting of a dense silicone-based top-layer of submicron thickness and a porous substructure containing macrovoids.[20,159–161] The membrane has been linked to a Membrane Products Kyriat Weitzman (Israel) patent, in which a cross-linked PAN support was treated with silanol-terminated polysiloxane as a pore protector, prior to applying the silicone coating, as discussed above. In order to cross-link the silanol-terminated PDMS, tetraethyl silicate and a tin-based catalyst were added to the coating solution.[26]

MPF-50 membranes were found to suffer from compaction,[20] which was partly reversible upon alternating pressures.[161] Such compaction can in the case of MPF-50 be attributed to the support layer, even though compaction of the dense silicone-based top-layer can not be excluded either, as stated above.[20,121] Machado and co-workers turned the measured solvent fluxes through MPF-50 into a model for solvent transport through SRNF-membranes.[160] Solvent flux through MPF-50 was found to decrease with increasing solvent polarity, while an opposite trend was noticed for the hydrophilic MPF-44 which was found to be even completely incompatible with hexane.[162] A same tendency was reported by Yang *et al.* for solvent transport through MPF-44, MPF-60 and MPF-50.[163] The same authors observed for the former two membranes significantly lower rejections in organic solvents than in water. This was attributed to the large sizes of the solutes in water due to coordination with surrounding water molecules. The lower rejections in ethanol and hexane compared to water for MPF-44 and MPF-50 have been explained by the enhanced mobility of polymeric chains in organic solvents.[162] Rejections of SelRo® membranes in organic solvents were generally found to be significantly lower than the manufacturer-specified MWCO-values, confirming that MWCO-values determined in a particular solvent are thus not useful to predict rejection properties in other organic solvents.[161]

MPF-50 has been tested in many applications, *e.g.* the recovery of organometallic complexes from DCM, THF and EA,[164] and of PTCs from toluene,[15,165] the separation of triglycerides from hexane[166] and for solvent exchange in pharmaceutical manufacturing.[167] Several more fundamental studies on solvent/solute transport mechanisms in SRNF have also been run on MPF-50.[20,21,159,161,162,168–178]

Starmem™ membranes. Another important class of commercial SRNF-membranes is the Starmem™ series, a trademark of W.R. Grace-Davison (USA) and distributed by Membrane Extraction Technology[179] (UK). The name of these membranes has been changed from the 142 series (3 membranes) to the Starmem™ series (4 types). These rather hydrophobic membranes are all PI-based and claimed to be stable in alcohols, alkanes, aromatics, ethers, ketones and esters. Starmem™ membranes have distinct MWCOs (based on 90% rejection of *n*-alkanes in toluene) of 200 Da (Starmem™ 120), 220 Da (122), 280 Da (228) and 400 Da (240). All membranes are available as flat sheets, pre-cut discs or spiral-wound elements.[179]

In contrast with MPF-50, soybean daidzin (416 Da) rejections were found to be lower in methanol, ethanol and acetone than in water.[169] Solvent fluxes for methanol–toluene and EA–toluene mixtures through Starmem™ 122 clearly decreased with gradually increasing toluene content.[173]

Different authors have used the Starmem™ membranes to study solute and solvent transport through SRNF-membranes,[19,169,173,180] or to apply them in catalytic applications. Dimethyl methylsuccinate was separated from methanol,[17] while homogeneous catalysts[15,181–185] and PTCs[15,165,186] were recycled. The membranes were also combined with chiral separations[187–190] and ionic liquid-mediated reactions.[191] Starmem membranes also proved useful in petrochemistry for solvent recovery in lube oil dewaxing[5,192] and aromatics enrichment,[5] in pharmaceutical manufacturing for solvent exchange[15,193] and microfluidic purification,[194] and could be used in membrane bioreactors (MBRs) for biotransformations.[195]

SolSep membranes. Since about 3 years, SolSep[196] (The Netherlands) has entered the SRNF-market, commercializing five NF-membranes with different stabilities and nominal MWCO-values (based on 95% rejection) between 300 and 750 Da, and one UF-membrane with a MWCO around 10000 Da. Chemical stability is claimed in alcohols, esters and ketones and for some membranes also in aromatics and chlorinated solvents. SolSep membranes are applicable at pressures and temperatures up to 40 bar and 150 °C respectively.[197] Permeabilities through the hydrophobic SolSep NF030505 membrane (MWCO not specified) for water, methanol and ethanol appeared significantly lower than the values obtained for MPF-50 [DE-S].[172] The SolSep-169 membrane was reported to combine high permeabilities for acetone [40 l (m^2 h bar)$^{-1}$] and EA (12) with rejections up to 91% for erythrosine B (880 Da) in acetone and 65% for Victoria blue (506 Da) in EA [CF-S].[191] SolSep 3360 was shown to have a top-layer of about 5 μm, clearly thicker than the barrier-layer of MPF-50. Consequenly, the ethanol permeability [1.2 l (m^2 h bar)$^{-1}$] was lower than for MPF-50 [5.2 l (m^2 h bar)$^{-1}$], while rejections for erythrosine B (880 Da) in ethanol were almost equal (92%) [CF-S].[198] Akzo Nobel recently reported filtration data for SolSep NF030306 in ethanol, *i*-propanol, hexane, heptane, cyclohexane, toluene, xylene and butyl acetate.[199]

HITK-T1 membrane. Important progress has been made in the development of ceramic membranes where German Hermsdorfer Institut für Technische Keramik[200] (HITK, Germany) recently brought the silylated TiO_2-based HITK-T1 membrane to the market.[157] With a nominal MWCO of 220 Da, this membrane showed methanol and acetone permeabilities around [0.4 l $(m^2 h bar)^{-1}$], while rejecting Victoria blue (506 Da) for 99% from methanol, and erythrosine B (880 Da) for 97% from acetone [CF-S].[171] Efficient catalyst recovery was reported with Pd-BINAP (849 Da) rejections around 94.5% [CU].[201]

3.7.2 Membranes designed for aqueous applications, but effective in SRNF. Desal-5 and Desal-5-DK, manufactured by Osmonics (USA), now GE/Osmonics, are PA-based hydrophilic membranes with a relatively dense structure, showing rejections for sucrose (342 Da) around 96%. According to Petersen, Desal-5 is a composite membrane consisting of a poly(piperazine amide) barrier-layer on top of a microporous PSf support between which an additional sulfonated PSf layer has been applied.[30] The chemical stability of Desal-5-DK in solvents has been reported to be limited, showing severe damage after exposure to EA and toluene. Desal-5 on the other hand remained intact with rejections for Solvent Blue (350 Da) of 9, 28 and 41%, in toluene, EA and methanol respectively [DE-S].[163] Desal-5 also performed reasonably well in the separation of oleic acid from methanol (>90% rejection) [CU],[166] and of Pd-BINAP (849 Da, 96%) and Wilkinson catalyst (925 Da, 93%) from DCM [DE-S],[164] while TOABr was only rejected for 55% from toluene at very low permeabilities [DE-S].[165] The role of solvent–membrane interactions for Desal-5-DK, as well as solute–membrane and solute–solvent interactions in water, methanol and ethanol has been studied for several solutes.[159,172] Desal-5-DK was shown to reject neutral solutes better in water than in organic solvents. For charged solutes, rejections were generally higher in water than in organic solvents.[169]

Besides the Desal membranes, other SRNF-membranes have been manufactured and commercialized, or at least made available for testing by Osmonics. Bhanushali *et al.* tested the aromatic PA-based Membrane YK, showing rejections for Sudan IV (384 Da) of 43% in hexane and 86% in methanol. With membrane D, a developmental PDMS-based membrane, rejections around 25% for the same dye were obtained, both in hexane and octane, while negative rejections were observed in methanol and ethanol [DE-S]. The triglyceride tripalmitin (807 Da) was rejected for 92% from hexane [CF-S].[178] Köseoglu *et al.* used the PA-based Sepa 0 (nominal MWCO of 500–1000 Da), Sepa 50 (MWCO around 600 Da), and the CA-based Sepa 97 membranes to separate cottonseed oil from ethanol, *i*-propanol and hexane. While the former membranes turned out to be damaged in hexane, almost complete rejection was measured for the latter, especially in hexane.[104] Filtration data for these membranes have also been reported by Schmidt and co-workers.[177]

4 Transport mechanism

4.1 Introduction

In order to understand and possibly predict fluxes and rejections for a certain membrane, the transport mechanism of solutes and solvents through porous or dense films of different SRNF-membranes should be thoroughly understood. This knowledge should by preference be integrated in readily applicable mathematical models, or alternatively be translated into clear, physico-chemically correct images, or even better a combination of both.

Basically three kinds of mathematical models can be distinguished to describe transport through SRNF-membranes. One group of models originates from irreversible thermodynamics, treating the membrane as a black-box. The two other groups of models take into account membrane properties. Starting at the MF-end of the spectrum of pressure-driven membrane processes, solvent transport occurs through the pores while solute separation relies on sieving. Several pore-flow models have thus been developed, in which the solvent and solute transport is empirically linked with feed viscosity, membrane pore size, *etc.* However, many of the tighter NF, and certainly all RO-membranes, are considered to have a dense top-layer, where only the free volume elements between the polymer chains allow transport. The transport and separation mechanism in these dense films thus has to be different and is generally described by the solution-diffusion model, originally developed by Lonsdale *et al.*,[202] or by a transient transport mechanism[203] – recently updated by Paul[204] – with characteristics from both the pore-flow and the solution-diffusion model.

First, the three groups of models will be shortly discussed in a more formal and mathematical way without too many details for which the reader is referred to some overviews of this matter.[2,205,206] A second part will describe in more detail the transport mechanism through the most studied membrane materials, like CA, PA, PI and PDMS. Finally, a special paragraph will be dedicated to transport through ceramic SRNF-membranes. To apply the transport models properly, the real interface concentrations should be taken into account, which are obviously not always easy to be determined.

4.2 The main types of transport models

4.2.1 Irreversible thermodynamics. *Basic principles.* A transport process is an irreversible process during which free energy is dissipated continuously and entropy is produced. This increase of entropy (S) can be calculated from the dissipation function ϕ, shown in eqn 1,

$$\phi = T\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_{\mathrm{i}} J_{\mathrm{i}} X_{\mathrm{i}} \tag{1}$$

where J_i and X_i represent the conjugated fluxes and forces, respectively, T the temperature and t the time. A linear relationship between fluxes and forces can be assumed when the system is close to equilibrium, as shown in eqn 2,

$$J_{\mathrm{i}} = \sum_{\mathrm{j}} L_{\mathrm{ij}} X_{\mathrm{j}} \tag{2}$$

where the sum includes all forces X_j acting on the system, while L_{ij} represent the phenomenological coefficients.

Kedem–Katchalsky and Spiegler–Kedem models. These two models, based on irreversible thermodynamics, have the same starting point, but the definition of the driving forces is different, respectively as differences or as differentials across the membrane. The Kedem–Katchalsky equations[207] (eqn 3), developed as early as 1958,

$$\begin{gathered}\Delta\mu_1 = V_1(p_\ell - p_0) + RT(\ln a_{1,0} - \ln a_{1,\ell}) = \\ V_1(\Delta p - \Delta\Pi)\ \Delta\mu_2 = V_2(p_\ell - p_0) + RT(\ln a_{2,0} - \ln a_{2,\ell})\end{gathered} \tag{3}$$

and adapted about a decade later to the Spiegler–Kedem equations[208] (eqn 4).

$$\begin{aligned}-\frac{\mathrm{d}\mu_1}{\mathrm{d}x} &= -\left(V_1\frac{\mathrm{d}p}{\mathrm{d}x} + \frac{\mathrm{d}\mu_1^{\mathrm{c}}}{\mathrm{d}x}\right)\\ -\frac{\mathrm{d}\mu_2}{\mathrm{d}x} &= -\left(V_2\frac{\mathrm{d}p}{\mathrm{d}x} + \frac{\mathrm{d}\mu_2^{\mathrm{c}}}{\mathrm{d}x}\right)\end{aligned} \tag{4}$$

Kedem and Katchalsky derived the following equations (eqn 5) for the volume flux J_v and solute flux J_s through a membrane:

$$J_\mathrm{v} = L_\mathrm{p}(\Delta p - \sigma\Delta\pi) J_\mathrm{s} = P_2\Delta c_2 + (1 - \sigma)J_\mathrm{v}\bar{c}_2 \tag{5}$$

The differential form of these equations (eqn 6) gives a more correct description of the solute flux, since the logarithmic average of the solute concentration used above, does not correctly reflect the difference in concentrations on both sides of NF- or RO-membranes.[154]

$$J_2 = -P_2\Delta x\left(\frac{\mathrm{d}c_2}{\mathrm{d}x}\right) + (1-\sigma)J_\mathrm{v}c_2 \tag{6}$$

The first and second term represent the contributions of diffusion and convection, respectively, while σ is the reflection coefficient, which can be interpreted as the fraction of solute reflected by the membrane in convective flow.

Maxwell–Stefan equation. To determine the driving forces in the basic equation of irreversible thermodynamics, the derivation of the Maxwell–Stefan equation starts from a force balance on the individual species:

$$\begin{gathered}\text{[driving force on a species i]} = \\ \text{[friction with all other species j]}\end{gathered} \tag{7}$$

After several assumptions, the generalised Maxwell–Stefan equation,[209] applicable for transport of multi-component mixtures through membranes, can be written as:

$$\begin{gathered}-x_\mathrm{i}\Delta_P\mu_\mathrm{i} - x_\mathrm{i}V_\mathrm{i}\Delta p - z_\mathrm{i}x_\mathrm{i}F\nabla\psi = \\ \sum_\mathrm{j}\left(\zeta_\mathrm{i,j}x_\mathrm{i}x_\mathrm{j}\left(v_\mathrm{i} - v_\mathrm{j}\right)\right) + \varsigma_\mathrm{i,m}x_\mathrm{i}v_i\end{gathered} \tag{8}$$

The total velocity v_i is considered here, which is the sum of a convective and a diffusive contribution. In porous systems, the convective contribution is dominant, while the opposite is true in dense membranes.

With $J_\mathrm{i} = v_\mathrm{i}x_\mathrm{i}C$, these equations can be adapted in terms of molar fluxes to:

$$\begin{gathered}-x_\mathrm{i}\Delta_P\mu_\mathrm{i} - x_\mathrm{i}V_\mathrm{i}\Delta p - z_\mathrm{i}x_\mathrm{i}F\Delta\psi = \\ \sum_\mathrm{j}\left(\varsigma_\mathrm{i,j}\left(\frac{\left(x_\mathrm{j}J_\mathrm{i}\right) - \left(x_\mathrm{i}J_\mathrm{j}\right)}{C}\right) + \varsigma_\mathrm{i,m}\frac{J_\mathrm{i}}{C}\right.\end{gathered} \tag{9}$$

4.2.2 Pore-flow model. The pore-flow mechanism supposes a constant concentration of the solute and the solvent over the membrane (Fig. 9). The difference in pressure across the membrane establishes a chemical potential gradient in both the pore-flow and the solution-diffusion models.

Based on a pure hydrodynamic analysis, the transport through porous membranes in the absence of a concentration gradient, can be described by Darcy's law (eqn 10) in which the permeability coefficient (k) contains structural factors, like membrane pore size, surface porosity and tortuosity.

$$J_1 = k\frac{(p_\mathrm{o} - p_\ell)}{\ell} \tag{10}$$

In the case of solvents, for which no significant concentration gradient is present in the porous membranes, the flux (J_1) is generally fitted with the Hagen–Poiseuille equation (eqn 11),

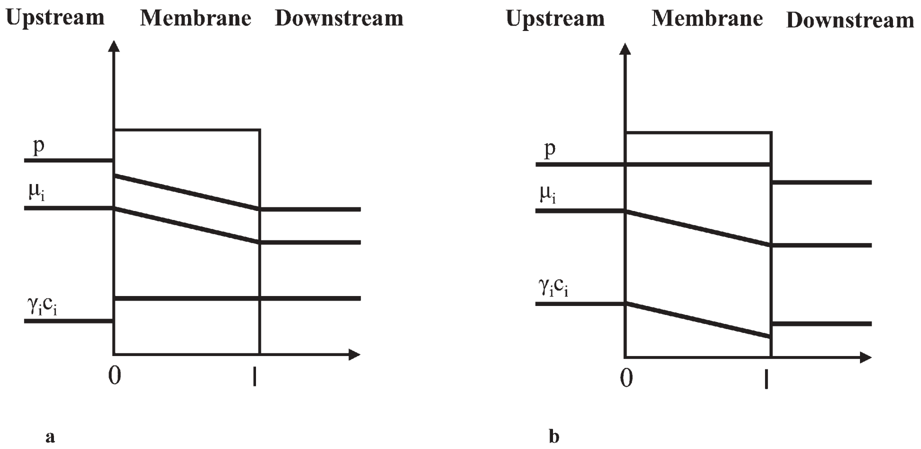


Fig. 9 Pressure-driven permeation of a one-component solution through a membrane according to: (a) pore-flow model and (b) solution-diffusion model (adapted from ref. 203).

in which viscosity (η) is an evident solvent parameter. However, a complication arises in SRNF, as pore size might depend on the type of organic solvent used, due to different swelling of the membrane polymer.[210]

$$J_1 = \frac{\varepsilon r_p}{8\eta\tau}\cdot\frac{\Delta p}{\ell} \tag{11}$$

For the solute flux (J_2), several empirical pore-flow models, based on the Maxwell–Stefan equation, have been developed. These models (eqn 12) make correlations between the hindrance factors $K_{2,\mathrm{d}}$ and $K_{2,\mathrm{c}}$ and the ratio λ of solute radius (r_s) to pore radius (r_p).[211]

$$J_2 = K_{2,\mathrm{d}}(\lambda)\ D_2\ \Delta c_2 + K_{2,\mathrm{c}}\ (\lambda)\bar{c}_2\ J_\mathrm{v} \tag{12}$$

Examples of such models are the Ferry, Verniori and Nernst–Planck models. These models indicate that the total solute flux comprises three fractions. The first fraction represents a diffusion process driven by a concentration gradient, the second an electromigration driven by an electric potential. A third fraction is the convection of solutes with the total volume flux. Bowen *et al.* developed a hybrid model based on the extended Nernst–Planck equation:[212]

$$J_2 = -K_{2,\mathrm{d}}D_2\frac{\mathrm{d}c_2}{\mathrm{d}x} - \frac{z_2c_2K_{2,\mathrm{d}}D_2}{RT}F\frac{\mathrm{d}\psi}{\mathrm{d}x} + K_{2,\mathrm{c}}c_2J_\mathrm{v} \tag{13}$$

Based on RO-experiments, where solute–membrane interactions are important, two other pore-flow models were developed, combining two factors that were found to determine the separation of a solute/solvent system in RO: (1) a distribution of the solutes at the membrane surface, involving interfacial forces between solute and membrane material, and (2) a kinetic effect, concerning the mobility of the solute relative to that of the solvent while permeating through the membrane pores. Based on these two factors, the surface force pore-flow model[213] and the finely porous model were developed.[214] Both models can be represented by a same type of equation:

$$J_2 = \frac{RT}{\varsigma_{1,2}b}\cdot\frac{\mathrm{d}C_2^\mathrm{m}}{\mathrm{d}x} + \frac{C_2^\mathrm{m}\cdot v_1}{b}\ \text{with}\ b = \frac{\varsigma_{1,2}+\varsigma_{2,3}}{\varsigma_{1,2}} \tag{14}$$

The solute flux is again composed of two fractions: (1) a diffusion process driven by a concentration gradient, and (2) the convection of solutes with the total volume flux. The third fraction, involving the electromigration of solutes, should evidently only be taken into account when an electric potential is applied, which is normally not the case in SRNF. The friction coefficients $\varsigma_{1,2}$ between solute (subscript 2) and solvent (subscript 1), and $\varsigma_{2,3}$ between solute and membrane (subscript 3) are reciprocally related to the diffusion coefficient of the solute in the solvent and the membrane respectively, and embody the kinetic effect or the solute mobility.[206] The surface force pore-flow and the finely porous model only differ in the description of the distribution of solutes at the membrane–feed solution interface. According to the finely porous model (eqn 15), the solute concentration C_2^m in the membrane is correlated to the feed (x = 0) and permeate (x = l) concentration by the solute distribution coefficient K_2, which is also present in the solution-diffusion model (see below):

$$x = 0\text{: } C_{2,0}^\mathrm{m} = K_2C_{20}^\mathrm{S}\mathrm{x} = \ell\text{: } \mathrm{C}_{2,\ell}^\mathrm{m} = K_2C_{2\ell}^\mathrm{S} \tag{15}$$

The surface force pore-flow model (eqn 16), on the other hand, correlates C_2^m to the feed and permeate concentration as follows:

$$\begin{aligned} x=0: &\qquad C_{2,0}^\mathrm{m} = C_{20}^\mathrm{s}\cdot\exp\left(\frac{-\phi(r)}{RT}\right)\\ \mathrm{x}=\ell: &\qquad C_{2,1}^\mathrm{m} = C_{2\ell}^\mathrm{s}\cdot\exp\left(\frac{-\phi(r)}{RT}\right) \end{aligned} \tag{16}$$

where $\phi(r)$ represents a potential function expressing the force exerted on the solute molecule by the pore wall or the membrane surface. $\phi(r)$ is a function of the distance r between the pore wall or membrane surface and the solute molecule. A positive $\phi(r)$ value represents a repulsive force, a negative value an attractive force. The force can be related to the distribution coefficient K_2,[215] which can be measured by HPLC using membrane polymer as the column material[216] or by sorption experiments.[217] Whenever $K_2 < 1$, the solute is repelled from the membrane resulting in a high solute rejection. A value above 1 on the other hand, means that the solute concentration of the interfacial solution exceeds the one in the feed solution, and is thus accompanied by low solute rejections. When $K_2 \gg 1$, the solute tends to adsorb strongly on/in the membrane.

4.2.3. Solution-diffusion model. For membranes in which the solution-diffusion mechanism prevails, free-volume elements are present as statistical fluctuations that appear and disappear in about the same time scale as the motions of the permeants that pass the membrane. Nomenclature-wise, these free-volume elements are thus different from 'pores' which are supposed to be fixed in time and space. However, both terms have been used in literature to describe the same, partly due to the fact that they come out of the mathematical models in an equivalent way. According to the solution-diffusion mechanism, only a concentration gradient exists as a driving force in the membrane. Such a dense membrane transmits pressure in the same way as a liquid (Fig. 9).

Following the assumptions made for solution-diffusion, a model was developed in the early seventies.[203]

$$J_\mathrm{i} = \frac{K_\mathrm{i}D_\mathrm{im}}{\ell}\left(1-\mathrm{e}^{\frac{-V_\mathrm{i}(\Delta p-\Delta\pi)}{RT}}\right) \qquad \text{with}\ K_\mathrm{i} = \frac{\rho w_\mathrm{i}^*}{w_\mathrm{m}M_\mathrm{i}} \tag{17}$$

Two simple equations could be derived for solute and solvent flux:[203]

$$\frac{J_1 = D_{1,\mathrm{m}}K_1c_{1,0}V_1(\Delta p-\Delta\pi)}{\ell RT}$$

$$J_2 = \frac{D_{2,\mathrm{m}}K_2}{\ell}\left(C_{2,0}^\mathrm{S} - C_{2,\ell}^\mathrm{S}\right)$$

This solution-diffusion model, with traditional approximations, has limitations. Important are the effects of coupling between solute and solvent, the so-called convective effects, which were clearly observed by Stafie *et al.*[8] and Bhanushali *et. al.*[178] Therefore, Paul revisited the mathematics of the solution-diffusion model using the ternary Maxwell–Stefan equations as a starting point:[204]

$$n_1 = \frac{\rho D_{1\mathrm{m}}}{\bar{w}_\mathrm{m}\ell}(w_{10} - w_{1\ell}) \tag{19}$$

$$n_2 = \frac{\rho D_{2\mathrm{m}}}{\bar{W}_\mathrm{m}\ell\left(1 + \varepsilon_2 \frac{\bar{w}_1}{\bar{w}_\mathrm{m}}\right)}(w_{20} - w_{2\ell}) \frac{\left(\varepsilon_2 \frac{\bar{w}_2}{\bar{w}_\mathrm{m}}\right)}{\left(1 + \varepsilon_2 \frac{\bar{w}_1}{\bar{w}_\mathrm{m}}\right)} n_1 \tag{20}$$

The equation describing solvent flux (eqn 19) comes down to the original one (eqn 17). With two fractions (diffusion and convection) in the equation that model the solute flux (eqn 20), this reformulated model has an analogy with equations originating from the finely porous model and the surface force pore-flow model. The main difference is situated in the fact that the latter models still assume a pressure gradient in the membrane and a Hagen–Poiseuille type of solvent flow. Taking into account this analogy between the latter three models, one can say that the pore-flow and solution-diffusion models match. Two mechanisms for solute transport through polymer films can thus be discerned: (1) *via* diffusion, which depends on the diffusion coefficient and the concentration gradient, and (2) *via* convection, which depends on the frictional coupling coefficient and the solvent flux. Considering the changing contributions of these two mechanisms to the overall solute flux in SRNF, solute migration can best be described by a transient mechanism.[203]

4.3 Detailed description of the separation mechanism for some selected SRNF-membranes

4.3.1 Cellulose acetate and polyamide membranes. The surface force pore-flow model was used to explain solute separations in methanol and water. In the case of hydrocarbon solutes, the strong adsorption ($K_2 \gg 1$) on the membrane surface and the concomitant agglomeration of the solute enhances separation from aqueous solution.[218] The friction for cations with high charge density is higher in methanol than in aqueous solutions, due to higher interfacial solvation in methanol and thus more steric repulsion. The opposite is noticed for cations with low charge density.[218]

Koops *et al.* investigated the separation of linear hydrocarbons and carboxylic acids from ethanol and hexane solutions with CA membranes.[219] Rejection was clearly shown to be solvent dependent as hydrocarbons were better retained in ethanol than in hexane. This observation was mainly explained by a higher ethanol flux, due to the higher affinity of this solvent for CA. Bhanushali *et al.* compared the Sudan IV (284 Da) rejection in methanol and hexane using the PA-based Membrane YK (see above). Again, a higher rejection was measured with methanol, *i.e.* the solvent with the highest affinity for the membrane material and thus the highest flux.[178] Indeed, according to the Spiegler–Kedem equations, higher solvent fluxes result in higher rejections. Carboxylic acids showed a negative rejection in hexane, because preferential interaction ($K_2 > 1$) of the carboxylic acids with CA took place while hexane had no affinity at all for CA.[219] Similar observations were made for the separation of aqueous phenol solutions with CA and PA membranes, where the phenol concentration in the permeate exceeded the one in the feed.[206,220,221]

4.3.2 Polyimide membranes. Iwama *et al.* studied different solvent fluxes through a PI-based UF-membrane showing a nice correlation with pressure and viscosity according to the Hagen–Poiseuille equation.[222] Silva and co-workers successfully applied both the two-parameter Hagen–Poiseuille model and the solution-diffusion model to predict the flux of toluene–EA solvent mixtures through the Starmem™ 122 membrane. Only the latter model allowed accurate prediction of the flux of methanol–toluene solutions.[173] Taking concentration polarization into account as well as the non-ideality of the solution at the membrane surface, the predictions by the solution-diffusion model were improved for docosane and TOABr separation from highly-concentrated toluene solutions using the same Starmem™ 122 membrane.[18] The separation of mixtures of alkanes and aromatic compounds from toluene with PI (Lenzing P84) membranes indicated preferential transport for the aromatic compounds. Calculation of the K_i/ℓ values from experimental data and the use of eqn 17, allowed predictions concerning aliphatic/aromatic separations in toluene with this type of PI membranes.[223]

4.3.3 Polydimethylsiloxane membranes. In terms of understanding transport and separation mechanisms in organic solvents, commercially available and laboratory-made silicone membranes have by far been the most studied. Most studies investigated the solvent and solute transport separately.

Machado *et al.* pioneered the field of solvent transport through SRNF-membranes.[160,224] By studying a large group of solvents and solvent mixtures, a resistance-in-series model was developed for MPF-50 (eqn 21), identifying resistances to viscous flow in both top-layer and porous support, and a hydrophilic/hydrophobic resistance at the membrane surface as the major mass transfer resistances.

$$J_1 = \frac{\Delta P}{\phi[(\Delta\gamma + f_1\eta) + f_2\eta]} \tag{21}$$

The viscosity (η) and the difference between the surface tension of solvent and membrane ($\Delta\gamma$) were incorporated as parameters determining solvent transport. f_1, f_2 and ϕ are fitting parameters representing membrane characteristics and mass transfer coefficients.[160]

Bhanushali *et al.* suggested a type of pore-flow model to describe the solvent flux through the silicone-based Membrane D, with also solvent viscosity and surface tension as important parameters. To improve the fit with the experimental data, another adjustable empirical parameter was added representing the sorption value for the solvent.[225]

The availability of laboratory-prepared PDMS membranes allowed the measurement of exact solvent swelling in the PDMS top-layer only.[20] The pure solvent flux correlated very well with the swelling/viscosity ratio, as confirmed later by Stamatialis *et al.*[16] Although the strongest influence was clearly exerted by the swelling, viscosity explained differences in fluxes for solvents with similar swelling. With almost no correlation between the solvent flux and the (molar volume)/viscosity ratio,[20] the observations for these PDMS membranes differ completely from the MPF-50 data, where apart from water and methanol, solvent fluxes increased nicely with the reciprocal viscosity.[160]

Dijkstra and co-workers modelled permeation results of various pentane/decane and pentane/dodecane mixtures through dense PDMS/PAN membranes with the solution-diffusion with imperfections model and the Maxwell–Stefan transport equation, taking into account both diffusive and viscous flow. Increasing pentane concentrations in the feed solutions reduced the contribution of diffusive flow due to increased membrane swelling.[226]

Robinson *et al.* systematically measured the solvent flux through a PDMS/PAN membrane for a wide range of hydrocarbons, including normal, branched and cyclic alkanes.[227] Within each group, the Hagen–Poiseuille model (eqn 11) fitted the data, showing linearity between solvent flux and the ($\Delta p/\eta$) ratio. Interestingly, each group showed another gradient $\varepsilon r^2/8\ell\tau$, explained by the change of membrane porosity upon swelling, since a relation existed between the calculated gradient and the Hildebrand solubility parameter. From these solubility parameters, a high swelling could be expected, hence increasing the membrane free volume and leading to some pore-flow type behavior. A pressure-dependent membrane transport mechanism was suggested for these 2 μm thick PDMS membranes: solvent flux was governed predominantly by hydraulic conditions at pressures above 3 bar, whereas solution-diffusion was apparent at lower pressures.[227] For the solute transport, three regions were observed: (1) a region where the solution-diffusion model applied, (2) another with a pore-flow regime, mainly indicated by the low rejection of the solute and (3) a transition zone with properties of both. Which mechanism actually prevailed, depended on the membrane swelling and the molecular size of the solute.[114,115]

Concerning the solute transport, Bhanushali *et al.* investigated the separation of several solutes from methanol, ethanol and hexane with membrane D.[178] The rejection was dependent on the solvent type: rejection of Sudan IV (380 Da) in hexane was about 25% while in methanol a negative rejection (−10%) was observed [DE-S]. Similar to CA and PA membranes, the negative rejection was explained by the preferential sorption and transport of the organic dye in the membrane. Coupling of solvent and solute transport, indicative for convective transport, was found to reduce with increasing solute size.[178]

Stafie *et al.* reported the separation of oil from hexane[8] and TOABr from toluene[16] with PDMS/PAN membranes. A significant influence of the solute concentration on the permeate flux was found due to the changes in osmotic pressure. Non-ideality of the TOABr/toluene system, indicated by a lower value of the osmotic pressure than calculated by the Van't Hoff equation, was explained by ion-pair clustering of TOABr molecules,[16] as stated above. Solvent–solute flux coupling was found to be dependent on membrane swelling, solute size, feed concentration and cross-linking degree of PDMS.[8,16]

Gevers *et al.* determined (alcohol/PDMS) distribution coefficients for several solutes with MWs between 300 and 1000 Da, showing the importance of solute charge, on top of the evident general role of solute size.[12] In actual membrane permeations, solute charge remained an important factor for smaller molecules, while steric considerations became dominant for larger solutes. The convective contribution to the solute transport, interpreted as solvent 'dragging', was found to be function of the size of the solute with respect to the size of the free spaces in the swollen polymer. Hence, the contribution of convective transport was most important for the smaller solutes in strongly swelling solvents. For *i*-propanol, toluene and methanol, the existence of bulk phase solvent in the membrane, either in the shape of clusters or as a real continuous phase was proven by differential scanning calorimetry, providing an explanation for the observed role of solvent viscosity on solute diffusion.[12]

4.3.4 Ceramic membranes. Irrespective the composition of the oxide (Al/Zr, Si/Zr, Si/Ti), ethanol fluxes through ceramic membranes were always higher than heptane and especially toluene fluxes. For the latter, long-range molecular ordering in the micropores was suggested. Even though not thoroughly investigated, it was concluded that the Si/Ti-based membrane was best adapted for paraffinic solvents, the Al/Zr for polar and the Si/Zr for aromatic solvents.[172]

An interesting fundamental study was performed on Si/Zr membranes with MWCOs of 200, 600 and 2000 Da applied in the filtration of aqueous feeds containing a wide variety of organic solvents and solutes. The Spiegler–Kedem equation was applied successfully to distinguish the contributions of diffusion and convection. With increasing temperature, permeabilities increased most for the largest solutes and the smallest membrane pores, with activation energies up to 30 kJ mol^{-1}. Solute diffusion through the membrane pores thus proved to be a clearly activated process, even for molecules as small as water.[154] A viscous flow mechanism was no longer applicable for alcohols permeating through pores smaller than 5 nm.[142] Only after conversion of the OH-functionalities of the pores into hydrophobic trimethylsiloxane moieties, membrane transport again obeyed viscous flow in ethanol. Without modification, alcohol adsorption on the silanol groups was suggested to reduce the effective membrane pore size.[153,228] Solutes, like *e.g.* decane, slowed down ethanol transport due to pore plugging.[153] The problem of limited long-term stability of silica membranes with small pores, as observed in PV at temperatures above 100 °C, seems to be absent after the above-mentioned modification and when applied in organic solvents, even at elevated temperatures.[229] So, in spite of the fixed pores and non-swelling matrix of ceramic membranes, solute interactions with the permeating solvent and with the membrane surface clearly need to be considered here as well. Moreover, as the pores in ceramic membranes get smaller and smaller, pore wetting becomes more important, thus emphasizing the role of solvent–membrane interactions.

5 Applications

5.1 Introduction

SRNF has the potential to be applied in a variety of industrial processes, in lab-scale organic synthesis and in the more fundamental unravelling of chemical reactions. The last two groups of applications have been touched only occasionally as yet, but the first has meanwhile been amply documented.

The introduction of better technologies, like *e.g.* SRNF, for work-up or post-reaction processing and separation, will yield significant environmental and cost benefits in solvent intensive processes.[15] It is thus as an alternative – or at least as a complement in a hybrid process – for distillations, evaporations, chromatographical separations, crystallizations, adsorptions or extractions, that SRNF has most potential. On top of the expected gain on the level of solvent use, significant energy savings can be anticipated as well. Most potential SRNF-applications studied so far involve processes with an immense economic impact, so a large part of the research has appeared in patent literature. It has mainly been the work on edible oil processing and petrochemical applications that has been IP-protected, and to a lesser extent the pharmaceutical and catalytic applications.

5.2 Food applications

5.2.1 Introduction. Most processes in the food industry are evidently aqueous, but in some cases the use of organic solvents is required. For treatment of aqueous streams, around 300,000 m^2 of NF-membranes are assumed to be currently applied already in the food industry, mainly in the dairy and sugar industry.[230] Solvents are in first instance applied in the vegetable oil industry, where acetone (for triglyceride fractionation) and especially hexane (for oil extraction) are often used, and in the synthesis of some food additives. Initial studies as early as in the 1980s resulted in several large-scale trials, but the disappointing results have cooled down the enthusiasm of researchers in the field for a long time. However, the large potential of membrane applications combined with new developments, re-initiated SRNF-research in this field over the past years. The main motives are the possibility to separate molecules in a customized manner, recycle solvents, reduce waste, minimize thermal damage and lower energy consumption.[47]

5.2.2 Edible oil processing. With a total annual world production of more than 380 million metric tons, edible oil production from seeds is a huge industry. Crude vegetable oils are commonly prepared by pressing the seeds mechanically, followed by a solvent extraction, mostly with hexane. The pressing step is eliminated for seeds with low oil contents, such as soybean and sunflower seeds.[231] The oil fraction contains over 95% of triacylglycerides, while the remaining components form a complex mixture of phospholipids, free fatty acids (FFA), pigments, sterols, carbohydrates, proteins and their degradation products. As these substances may shorten shelf-life, or impart undesirable flavor and color, crude oil needs further refining.[232]

Refining conventionally consists of 4 steps (Fig. 10): (1) 'degumming' to remove the phospholipids, (2) neutralization of the FFAs with NaOH to produce soaps, (3) adsorption of pigments on acid-activated bleaching clays or carbon, and (4) steam distillation under high vacuum to strip traces of volatile compounds. The whole process is extremely energy-intensive, produces solid wastes and polluted effluents, and suffers from substantial oil losses.[231] There are several steps in edible oil processing where integration of membrane technology offers opportunities by replacing – or at least supplementing – conventional approaches: the removal of phospholipids and pigments (degumming), the recovery of extraction solvents and the deacidification of the oil (Fig. 10). It has been estimated that introduction of membrane technology in edible oil processing could potentially save 15–22 trillion kJ per year of energy in the USA alone,[231] while reducing oil losses by 75%, improving the oil quality, and minimizing thermal damage. Moreover, nutrients would be better retained, and no longer would addition of chemicals be needed, thus reducing waste streams.[233] In an attempt to recover valuable products like carotenoids (536 Da) from red palm methyl esters, several commercial SRNF-membranes have been evaluated in a multi-stage membrane process. The separation of the carotenoids removed the undesired color from the oil product

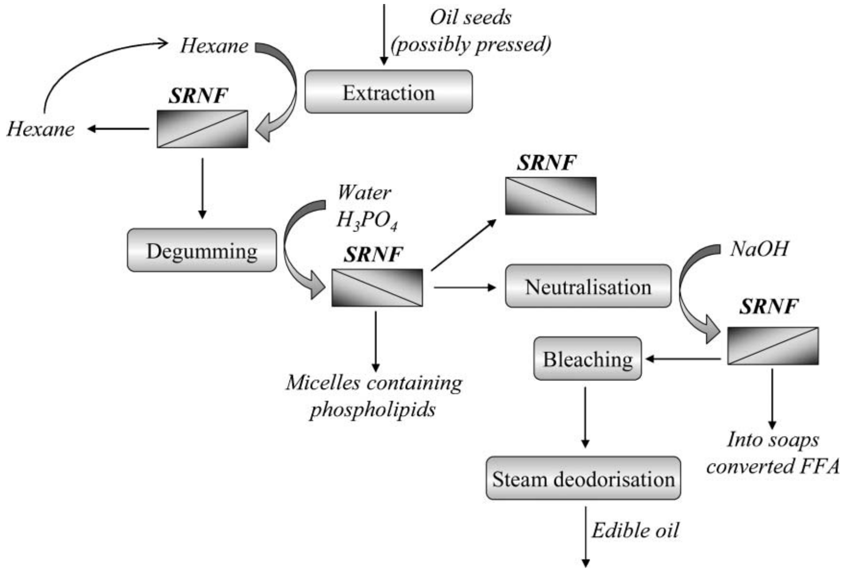


Fig. 10 General scheme for edible oil processing with possible opportunities to implement SRNF.

and created a valuable natural product for use in nutraceuticals and cosmetics.[234]

Degumming. The removal of phospholipids from the crude oil is the most studied process for which a mere solvent resistant UF-membrane would in fact be sufficient. Degumming conventionally occurs by hydrating the phospholipids to an insoluble form and centrifuging them. In apolar solvents, the amphiphilic phospholipids form reversed micelles, trapping the more polar components inside. These micelles with a MW around 20 kDa are easily filtered from the oil and the solvent that form together the continuous phase. The liquid is referred to as 'miscella' and contains 70–75% of solvent.[232] In a Lever Brothers (now Unilever) patent, the phospholipids were completely removed by using a dense silicone SRNF-membrane, while removal down to only 16 and 23 ppm was realized with a PSf (MWCO 10 kDa) or a PAN-based UF-membrane (MWCO 50 kDa) respectively [CU]. In addition, the color of the crude oil was lowered and the metal content reduced. The silicone membrane was considered best, despite a certain triglyceride rejection and a lower permeability.[235] Similar data were reported using the Osmonics DS-7, also a silicone-based membrane, showing almost complete phospholipids rejection, unfortunately combined with 35% oil rejection [CF-S].[232]

Problems in the degumming process mainly arise from membrane fouling by the retained micelles. PVDF membranes were shown to be considerably more fouling-resistant than PES and PSf membranes.[236] Using ceramic UF-membranes, several operational parameters for the degumming filtration process have been studied in detail. Even though the rejection with an alumina anodisc membrane (0.02 μm pore diameter) was very low, the accumulation of phospholipids at the membrane surface induced severe concentration polarization and gel layer formation.[237] The latter was also found in degumming with a PI-based UF-membrane.[238] In addition to membrane fouling, mass transfer problems have also been reported on the level of the spacers separating the individual membranes in industrial membrane modules. High resistance to the passage of the viscous miscella has been observed. In combination with spiral wound modules, PI-based tubular membranes (20 kDa MWCO) were able to remove 99.9% of the phospholipids [CU].[239]

Possible solvent stability issues of membranes used for degumming can be overcome *via* direct degumming of vegetable (non-extracted) oil, as obtained from pressed seeds. A major difference as compared to solvent-based degumming and at the same time also the major bottleneck of this alternative process is the low permeability of the membrane for triglycerides (in this case the solvent phase), which on average is about one order of magnitude lower than for solvent-based degumming. However, the absence of solvent and related energy, safety and environmental issues might make the process competitive.[230]

Recovery of extraction solvents. Extraction solvents are normally recovered by distillation to increase the oil content to about 90%. This goes along with an estimated solvent exhaust to the environment of several tens of thousands of tons of solvent per year.[240] To improve environmental, safety and economical aspects of the edible oil processing, SRNF is an attractive alternative to retain the oil fraction. In most cases, the concentrated oil fraction of the retentate should still be further purified by distillation, but less energy is obviously required. An interesting new opportunity might be created by the introduction of SRNF in oil concentration prior to degumming: since the solvents no longer need to be volatile, new solvents could be introduced for oil extraction. Ketones and alcohols for instance could thus enhance extraction yields, keeping the process environmentally friendly and safer.[240]

Commercial RO- and NF-membranes have been screened in the separation of oil from different solvents. CA, PVDF and PA membranes all showed acceptable performance in *i*-propanol and ethanol, but were either damaged in hexane or showed low permeabilities.[104] A cross-linked PDMS membrane has been used in the separation of oils from hexane and *i*-octane, with a high permeability and rejection values of 90% [CU].[241] Stafie reported similar rejection values for laboratory made PDMS membranes [DE-S].[7] To avoid membrane damage by hexane during the filtration of hexane-extracted soybean oil, a ceramic anodisc membrane has been used. With pore diameters of 0.02 μm, only 20% rejection could be reached with this membrane, and even then feed side stirring was needed to prevent mass transfer problems [CF-S].[237] Oleic acid was retained for 93% and 96% from hexane and methanol respectively by PA membranes that were hydrophobised by mixing PDMS with the monomers [CF].[106,107]

Ketones are in use already to fractionate triglycerides for specific purposes. The removal of acetone *via* evaporation from such fractions obtained *e.g.* from cocoa butter, partially degraded the product. To lower the impact of the process on the oil quality, a room temperature membrane separation could be a nice solution to remove at least part of the solvent.[240]

Deacidification. The last step in edible oil processing with potential membrane application is the removal of FFAs from the crude oil fraction. This is classically done by alkali-refining. As it is an energy-intensive operation involving the use of large quantities of water and chemicals and possibly leading to losses of neutral oils, many new approaches are currently being investigated.[242]

Sunflower oil has been separated from the free oleic acid molecules with a commercial silicone-based membrane.[233] The selectivities of this very demanding separation combining a total rejection of a 700 Da compound with the full permeation of a 300 Da compound, are too low for industrial use, and so are the fluxes of these rather viscous feeds.[242,243] When the feed was diluted with hexane, viscosity was obviously less problematic. The triglyceride extract was then treated with the SRNF-membranes to retain the triglyceride with coupled permeation of solvent and FFA.[243] With PEBAX and cellulose-based membranes, almost pure FFAs could be obtained in the permeate. When a significant amount of FFA remains in the retained oil fraction, further processing is required.[244]

An alternative way to deacidify is to apply first an extraction with an organic solvent with good selectivity for the FFAs, *e.g.* methanol, followed by a membrane filtration to remove the

FFAs from that extraction solvent.[242,245] RO-membranes like Desal-5 (GE/Osmonics) and NTR-759 (Nitto Denko) were able to remove oleic acid from methanol with rejections above 90% [CU].[166] An important problem associated with high rejection membranes is the significant drop in flux, especially when concentrated solutions are processed. A combination of high rejection and low rejection membranes seems a good solution to end up with higher concentrations. Raman *et al.* suggested a multi-stage membrane system to increase the overall FFA-recovery.[166] A hydrophilic GKSS membrane showed promising selectivities to remove FFAs from an oil/acetone mixture, but the FFA-fluxes were still too low. Moreover, long-term stability needed improvement as the membrane lost its hydrophilic character due to polarity conditioning.[243]

5.2.3 Synthesis of amino acids and derivatives. Besides in edible oil processing, the use of SRNF has been studied in food technology in the synthesis of amino acids and their derivatives. The production of dipeptides, like L-aspartyl-L-phenylalanine methyl ester, better known as aspartame, is based on an enzymatic process in organic solvents. The limited stability of the enzymes turns membrane separations into an interesting alternative. The dipeptides are prepared from amino acids or their derivatives. After reaction, the unreacted amino acids should preferably be recycled to make the process more performant. Reddy *et al.* tested several commercial CA, PI and PA membranes in different solvents, and found the Toray PA/PPSf composite membrane to be the most promising to recover the unreacted amino acid derivatives from methanol. However, butyl acetate and 2-methyl-2-butanol are the preferred solvents for this type of reaction, so further research is necessary to apply other membrane materials that are more resistant and better performing in these two solvents.[246]

5.2.4 Concentration and purification of bio-active compounds. A membrane-based method to purify and concentrate xanthophylls from ethanol extracts of corn was recently reported.[247] Xanthophylls are yellow-orange oxygenated pigments of the carotenoid family, valuable as natural colorants or as nutraceuticals. UF was used to separate co-extracted ethanol-soluble proteins and other large solutes from the extract, after which the xanthophyll-containing permeate was concentrated and separated from the solvent using NF. Different commercial UF- and NF-membranes were screened, of which Desal-DK performed best in terms of flux, rejection and stability.[247] In another study, desalination membranes have been applied to separate caffeine from a group of catechins, known as polyphenols, originating from a mixture of bio-active components obtained *via* ethanol extraction of green tea.[248]

5.3 Catalytic applications

5.3.1 Introduction. The separation of reaction products from catalysts is a major problem in many types of homogeneous catalysis. A major drawback of such catalysis is the extensive and usually destructive post-reaction work-up needed to remove the catalyst from the reaction medium. At present, hardly any industrially used separation is aimed at the recovery of the catalyst in an active form, but rather at obtaining a pure product whilst recovering the metal in a form that may be recycled to a catalyst manufacturer. Usually, homogeneous catalysts are relatively large (MW $>$ 450 Da), and the reaction products substantially smaller, so that separation is feasible with SRNF.[15,249] Important efforts have been made over the past years to separate homogeneous catalysts from their reaction mixtures in order to recycle the catalyst and/or facilitate product purification. With extremely active catalysts, like *e.g.* certain Heck-coupling catalysts or Rh-based hydrogenation catalysts operating at substrate/catalyst ratios of far over one million, catalyst recycling might not be economically interesting. Moreover, with only some ppt-level contamination of the product, the catalyst removal is not even really needed anymore for health reasons if applied in pharmaceutical production. In all other cases, removal of homogeneous catalysts is currently most commonly done *via* distillation, chromatography or extraction.[250]

Due to the absence in the recent past of suitable SRNF-membranes for separations of homogeneous catalysts, a lot of effort in the literature has been devoted to the filtration of enlarged catalysts. Such enlargement obviously became less and less needed as more and better performing SRNF-membranes became available to separate the catalyst from the solvent and temperature conditions applied in the reaction. The membrane can then be used for the mere recovery and/or recycling of the catalyst, but the coupling of an SRNF-membrane to an ongoing homogeneous reaction can also help to increase reaction conversion, shorten reaction times and improve product selectivity.[251,252]

Whenever SRNF is chosen to recover homogeneous catalysts, very high catalyst rejections are absolutely necessary in order to be economically viable. This is shown in Fig. 11 where the total catalyst loss after an *n*-fold recycling is plotted for different rejection values.[253] Just a good catalyst rejection by the membrane on its own is however not enough to realize a successful recycling: also a long-term catalyst stability is needed. Quite often, such limited catalyst stability only

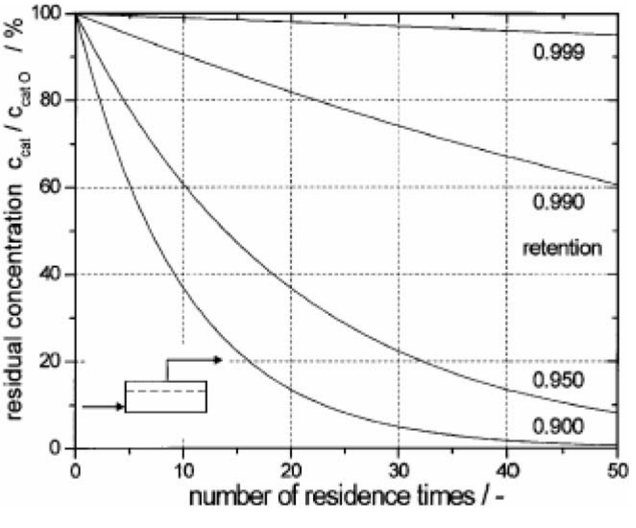


Fig. 11 Residual catalyst concentration as a function of the number of reactor residence times (taken from ref. 253).

becomes apparent from the moment that a membrane with a good selectivity has been applied for the recycling.[254]

If a membrane is not sufficiently resistant to the pressure and temperature conditions needed for reaction, continuous membrane reactors are excluded. Only a batchwise filtration-reaction cycle, in which reaction and filtration conditions can be optimized separately, can still be applied then. If the membrane can not resist the reaction solvent either, only a more complicated solution can solve this problem. A PDMS membrane of which the PAN support dissolved in NMP, a typical solvent for the studied Heck reaction, was made applicable by adding cyclohexane to the reaction mixture prior to filtration. After SRNF of this strongly diluted NMP-solution, the cyclohexane was removed again by evaporation.[255] Obviously, whenever possible, such extra procedures should be avoided from a practical and economical point of view, and the use of existing selective membranes with stability in demanding solvents such as *e.g.* NMP would be a better way out. When a cross-flow filtration is coupled to a catalytic reaction, the term 'loop reactor' has also been used by several authors.

5.3.2 Enlarged catalysts. Several approaches can be used to enlarge homogeneous catalysts to facilitate their separation during membrane filtration. A simple enlargement of the Rh-Wilkinson catalyst was realized by using ligands with long fluorinated spacers to reach a 2–4 nm size, clearly larger than the 0.6 nm pore size of the applied silica membrane (ECN, The Netherlands). Neither Rh, nor ligand was found in the permeate and the membrane was stable enough for use in the hydrogenation of 1-butene in supercritical CO_2 at 353 K under a pressure of 20 MPa.[256,257] In another approach to increase rejection of homogeneous catalysts, micelle forming amphiphiles were simply added to a Rh-catalysed hydrogenation reaction mixture. The hydrophobic ligand was well retained by the formed hydrophobic micelles, but the more hydrophilic metal permeated rather fast through the membrane.[258]

Strictly speaking, enlarged types of catalysts, such as dendrimers,[259] hyperbranched polymers[260] or catalysts bound to soluble polymers,[261] are also homogeneous catalysts. Dendrimers have been introduced in 1995 as high-MW, but monodisperse and well-defined catalysts.[262] Owing to their mostly globular shape, dendrimers have a lower intrinsic viscosity and better accessibility of the active sites compared to catalysts anchored to soluble polymers.[253] Their synthesis is however tedious and expensive, leading to only few commercial applications so far.[263] Hyperbranched polymers are a cheaper alternative for dendrimers, involving only a single-step synthesis. This goes at the expense of a higher polydispersity and a functionalisation that is distributed throughout the whole macromolecule.[260] With a MW sometimes far above 1000 Da, the separation of these enlarged catalysts is mostly not a real SRNF-problem anymore, but rather a UF- or MF-problem. However, their systematically increasing MW over subsequent generations starting below 1000 Da, and the use in literature of typical SRNF-membranes like MPF-50 to reject them, warrants some comments in this review. It should be taken into consideration that just enlarging the dendrimer does not necessarily imply strongly increasing rejections. Indeed, so-called backfolding of the dendritic branches can increase rejection less than anticipated, especially if the enlarged dendrimers get less shape-persistent. Also, the dendrimer shape and size might change with changing solution polarity.[264]

Especially when used in strongly swelling solvents, membranes as dense as NF-membranes were found to be really needed to retain dendrimers with MWs far in the UF-range. Applied in THF-based enantioselective reductions for instance, MPF-50 was used to retain 14 kDa catalysts.[265,266] Analogously, 10 kDa large dendrimers could be retained for 99.9% in DCM during an allylic substitution with a Pd-catalyst [CU-L-continuous]. Despite the good rejections, catalytic activity was still lost upon recycling due to the formation of inactive Pd-species.[253] Similar effects were observed for the same reaction type using MPF-60 in THF.[267] The catalyst decomposition could later be limited by changing the structure of the dendrimer.[254] A Ni-dendrimer of around 2 kDa was also retained by MPF-60 in a Kharash addition in DCM.[268] More successful Pd-catalyst recycles were realized in Sonogashira and Suzuki reactions when using PS coupled catalysts with MWs between 5 and 35 kDa. Even with the smallest catalyst, less than 0.05% Pd leached and no yield decrease could be observed after as many as 9 cycles [DE-L].[255]

In order to specifically limit product isomerisation in the Pd-catalysed vinylation of styrene, a dendrimer was prepared to allow the use of a continuous membrane reactor to be run at low conversion. A MPF-60 membrane was selected, but could only retain 85% of the dendrimer (1314 Da) in the styrene solution [CU-L-continuous]. A second generation dendrimer with increased MW was thus prepared. A much better rejection was realized, but decreasing catalytic activities were still observed on the long term, once again due to the formation of Pd black.[269]

In contrast to the commercial MPF-50 membrane, a laboratory-made zeolite filled PDMS membrane was found to retain porphyrin containing dendrimers well enough, even in strongly swelling solvents like chloroform. Chloroform was preferred for the studied photo-oxidation of olefins, since the generation of singlet oxygen from ground-state oxygen was most efficient in this solvent. The membrane resisted the highly reactive conditions of the reaction mixture. As the peroxides simply permeated through the membrane, their membrane purification was a huge improvement compared with the commonly applied distillation where the presence of peroxides creates hazardous conditions at the applied elevated temperatures and reduced pressures.[270]

5.3.3 Transition metal complexes. Already in 1973, an asymmetric PI membrane was used to synthesize organometallic compounds with enhanced catalytic activity. By removing the dissociated ligand from Ru-phosphine complexes, an active ligand-deficient complex was obtained. Being too unstable to be isolated as such, the authors succeeded in preparing the dinitrogen compound $RuH_2(N_2)(PPh_3)_3$ by using N_2 as the pressurizing gas. RO was thus used to replace a dissociated ligand (PPh_3) by a more labile one (N_2) in the synthesis of several new organometallic complexes.[271] It was only 4 years later that the same membranes were actually used in a catalytic process involving hydrogenations and hydrodimerisations with Ru-complexes, hydroformylations with Co- or Rh-complexes and carboalkoxylations with Pd-complexes. With pressures up to 95 atm, catalysts could be retained with varying degrees of success.[272]

Recycling off-the-shelf homogeneous catalysts was first claimed in a 1993 patent assigned to Membrane Products Kiryat Weitzman, but no data or specific examples were given.[26] Four years later, a Union Carbide patent described how a Rh-catalyst was retained for >99% and >93% in butyraldehyde and acetone respectively by an MPF-50 membrane during a hydroformylation [CU].[273] The first detailed open-literature study on SRNF-coupled reactions with non-enlarged catalysts dates from 2001 only and describes how Ru-BINAP and Rh-DUPHOS catalysts were retained by MPF-50 membranes in methanol for more than 97%. The hydrogen pressure needed during the hydrogenation reaction simultaneously provided the driving force for the filtration [DE-L-continuous].[274]

Mainly two classes of membrane types have been investigated with respect to homogeneous catalysis: PI asymmetric membranes and PDMS-based composite membranes. For the PDMS membranes, excessive membrane swelling upon contact with the reaction mixture was dealt with by adding porous fillers to the elastomer (see above). The availability of the USY-filled PDMS membrane enabled new catalytic applications, such as the hydrolytic kinetic resolution of epoxides with the Co-Jacobsen catalyst in diethyl ether, for which many other commercial membranes failed to combine reasonable fluxes and selectivities.[275] Due to reduced membrane swelling, improved performance of the commercial membranes was observed in *i*-propanol, but even then rejections never exceeded 93% [DE-L]. No good membranes were found to operate under solvent-free conditions, where the very high viscosity of the reaction mixture did not allow reasonable permeabilities. Interestingly, some of the tested membranes were actually marketed as PV-membranes, proving that SRNF- and PV-membranes can essentially be the same type of materials.[276]

The second type are the PI-based Starmem™ membranes manufactured by Grace-Davison. For the Pd-catalysed Heck coupling reactions, a trade-off was found with these membranes between good membrane separation and fast catalysis in the 3 solvents screened: the best solvents for catalysis did not allow sufficient rejection of the catalyst. The ammonium salt formed as a by-product during the reaction did not interfere with the membrane separation as it precipitated out and could simply be removed manually from the reactor after each subsequent filtration.[185] The major problem rendering catalyst recycling less efficient was again the formation of inactive Pd black species. Later on, chemically more robust Heck catalysts were found and combined with SRNF.[183] Addition of ionic liquids (ILs) to the reaction mixture had a positive effect on the catalytic stability.[181] In Suzuki cross-coupling reactions, undesired Pd black formation was prohibited and higher catalyst turnovers could be obtained this way.[182,191]

Addition of ILs also proved beneficial at the level of (enantio)selectivity, as shown for a Ru-BINAP catalysed hydrogenations. The catalyst rejections in this case however decreased slightly. From the Ru/P stoichiometry in the permeate it could be concluded that it was mainly a broken down catalyst that permeated through the membrane under the form of smaller pieces.[181] Apart from stabilizing catalysts, ILs are normally combined with catalysis to create a two-phase system. Reaction products then mostly end up in the ionic liquid phase, from which they are removed by distillation. For non-volatile compounds, SRNF can be a valuable alternative with either the organic compound or the ionic liquid permeating.[277]

For the recycling of PTCs in toluene with the same type of membranes, excellent fluxes and rejections were obtained. Flux decrease was observed during the filtrations and was ascribed to both compaction and concentration effects at the retentate side leading to catalyst precipitation. The latter occurred even clearly below the theoretical solubility limits of the retained compound. Most probably, counter-ion, product and reagent effects in the membrane boundary layer also played a role here. Simple washing of the membrane was sufficient to restore the original flux.[186] The Starmem™ membranes were all found to be much better performers, both flux and selectivity-wise, for this application than MPF and Desal membranes. Self-supporting silicone and EPDM membranes failed to give reasonable fluxes.[165]

For three solvents (DCM, EA, THF) and three types of catalysts (Mn-Jacobsen, Pd-BINAP and Rh-Wilkinson), a good membrane could be found for each solvent/catalyst combination, except for Jacobsen/DCM. In most cases, the Starmem™ membranes offered the best combination of flux and rejection.[164]

To a much lesser extent, ceramic membranes have been coupled to homogeneous reactions. A large self-assembled and shape-persistent polyoxometalate catalyst was very well retained by a γ-alumina membrane with 5 nm pores. Surprisingly, after each reaction/filtration cycle, the catalyst was found to be more active, which was ascribed to the removal of excess Aliquat 336.[278] Only one other type of ceramic membrane, a silicalite-based zeolite membrane, has been combined with homogeneous catalysis.[279] Ceramic membranes could form an elegant solution for the filtration of 'polymer aggressive' solvents, like DMA for instance. However, the described DMA-fluxes with this zeolite membrane were extremely low, suggesting the strong adsorption of the solvent in the zeolite pores. Better separations were obtained for the separation of a Pd-based Heck coupling catalyst from DCM.[279]

In order to further increase the metal removal in reactions catalysed by transition metal complexes, MET (UK) couples the SRNF to an unidentified adsorbent in their MEMSORB-process.[280]

Apart from the catalyst, also the ligands which are often even more expensive, can be recycled with SRNF. Lyondell Chemical Technology recently patented the use of a SRNF-membrane, exemplified by the hydrophilic MPF-44, to recover triphenyl phosphine from the reaction mixture, typically methanol–water, present during the production of propylene oxide from propylene, oxygen and hydrogen. The phosphine is needed to promote the reaction catalysed by a Pd-functionalised titanium silicate catalyst (TS-1-zeolite) which can be easily recovered as a solid from the reaction mixture. The promoter is retained by the membrane and can be sent back to the reactor, while all solvents, remaining reagents and formed products can permeate through the membrane.[281]

5.3.4 Catalytic nanoparticles. Another class of metal-based catalysts that have increased in popularity over the past years are metal nanoparticles, sometimes also called giant clusters, nanoclusters or colloids. Due to their very high specific surface, they are a powerful class of so-called 'semi-heterogeneous' or 'pseudo/quasi-homogeneous' new catalysts. This nomenclature refers to the fact that they should be, at least in principle, separated easily from their reaction mixtures by common filtrations. However, reality demonstrated how challenging this still is, especially when the particles get really small. In order to facilitate their removal, the colloids are often immobilized or grafted on inorganic or polymeric supports. Catalytic nanoparticles are commonly prepared from a metal salt that has been reduced, *e.g. via* reaction with $LiBH_4$, under specific conditions and in the presence of stabilizers, *e.g.* polymers.[282] The examples below all involve NF-membranes, even though – similar to enlarged catalysts discussed above – UF-membranes would be sufficient based on catalyst size only. However, strong membrane swelling, and the possible presence of smaller colloids or dissolved metal species and stabilizers in solution warrant the choice of NF-membranes, possibly at the expense of some flux.

Pd-nanoparticles protected with highly branched polyglycerols were used in the hydrogenation of cyclohexene (neat or toluene diluted) and recycled 30 times with the MPF-50 membrane. With particle sizes around 4.7 nm, the SRNF-membrane retained more than 99% of the total Pd over all cycles. Some limited Pd-deposition on the membrane did not lower catalyst activity [DE-L-continuous].[283] With PVA-stabilised 2–4 nm sized Au-colloids, water- and alcohol-based oxidation reactions of aliphatic diols were performed in combination with several membranes. In water, a CA membrane retained the catalyst better than a Desal-5-DK or a PI membrane, but membrane fouling occurred. Using *i*-propanol as reaction solvent, a PDMS-based membrane was able to fully retain the catalyst at high fluxes and without any fouling. After three recycles, some catalytic activity was lost, probably due to long-term catalyst deactivation [DE-S]. Tertiary butanol was applied as a solvent to allow oxidation of less polar alcohols as well. Here again, complete rejection of the catalyst and absence of membrane fouling was realized.[284,285] Quasi-homogeneous PVP-stabilized Ag– (4 nm) and Co-nanoclusters (20 nm), used for the dehydrogenation of α,ß-unsaturated aldehydes, were recycled with a custom-made PI-based SRNF-membrane. After cross-linking, the membrane proved sufficiently stable for the post-reaction separation of metal colloids from amidic media, the preferential solvent class for the studied reaction. Catalytic performance and colloidal stability were satisfactorily preserved upon recycling.[286]

5.3.5 Biocatalytic applications. Biotransformations play an increasingly important role in organic synthesis for the production of fine chemicals. An important number of substrates and products of biotransformations are poorly soluble in water, the medium in which most biocatalysts show optimal activity. This limits the possibilities to convert hydrophobic substrates at high concentrations. Direct-phase biphasic reactions might solve that problem, but the necessary strong stirring can cause irreversible emulsification, while the presence of the organic phase can inhibit the biocatalyst. The Starmem™ 122 membrane has been used in an alternative contactor set-up allowing organic phase to permeate to the catalyst containing aqueous phase. The proposed membrane bioreactor allows high substrate loadings and efficient product removal, and avoids inhibition of the biocatalyst activity by the organic phase. Emulsion formation was prevented and solvent toxicity mitigated, thus expanding the range of solvents that can be used as 'reagent source phase'. This was illustrated with a model reaction, the biotransformation of geraniol to R-citronellol by baker's yeast, performed in toluene and *n*-hexadecane, solvents in which the biocatalyst proved inactive in a conventional direct-contact biphasic reactor. However, the SRNF-based contactor set-up resulted in lower productivities than those observed in a direct-contact biphasic reactor due to limitations in the transfer rate of the substrate through the membrane.[195]

In a hybrid biocatalytic/chemocatalytic set-up, dynamic kinetic resolution was studied for cases where the catalytic conditions for resolution and racemization are not compatible. The two reactive systems were separated by a SRNF-membrane, allowing permeation of product and substrate, whilst retaining the (bio)catalysts (Fig. 12). The racemization and resolution reactions were catalysed by a Ru(cymene)/amine base system and a lipase respectively. The concept worked, but the Starmem™ 122 membrane degraded under the reported conditions due to limited base stability.[187]

5.4 Petrochemical applications

5.4.1 Introduction. The refining industry is both energy- and separations-intensive, and is often accompanied by a large exhaust of organic solvents, suggesting that large-scale membrane systems can provide significant benefits. Potential SRNF-applications in the petrochemical industry indeed include real large-scale processes. The separations are often extremely challenging, involving compounds to be separated with very similar molecular properties. The selectivities

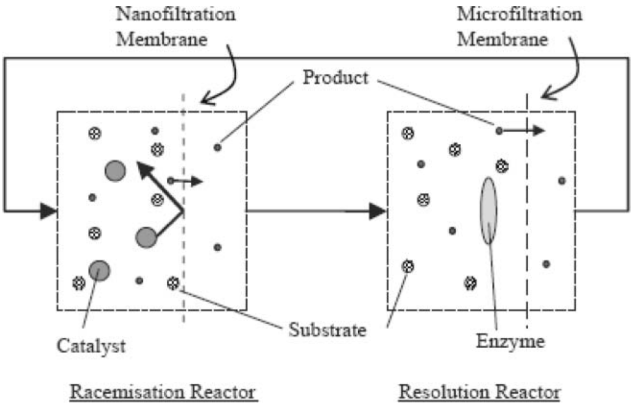


Fig. 12 Schematic representation of membrane-enhanced dynamic kinetic resolution (taken from ref 187).

mentioned in most patents are often quite low, and whether these are really sufficient to allow practical implementation often remains unclear. Anyhow, for most described applications, SRNF seems to be an interesting complement to facilitate or optimize an existing separation, more than to replace it.

5.4.2 Solvent recovery in lube oil dewaxing

The largest SRNF-plant running for years already (since 1998) at industrial scale is situated in the petrochemical industry. It is the Max-Dewax™ process at the ExxonMobil refinery in Beaumont (Texas) for the recovery of dewaxing solvents from lube oil filtrates.[192,287–292] The key to successful operation of this large-scale membrane-based solvent recovery process, handling 11,500 m^3 feed per day, was the integration with the existing process units. The application is a typical example of the 'de-bottlenecking' of a conventional process whose expansion was needed but practically limited, in this case by its refrigeration and solvent recirculation capacity. A typical solvent dewaxing process involves the incremental addition of a mixture of volatile solvents, usually MEK and toluene, to a waxy oil raffinate. This mixture is cooled to -10 °C and brought over rotating drum filters where the precipitated waxes are separated from the solvent stream (Fig. 13). The lube oil filtrate still contains some waxes and the solvent is removed from it by a combination of multi-stage flash and distillation operations. Prior to feeding the solvent back into the dewaxing process, it obviously needs to be refrigerated again.

In the late eighties, several groups initiated research to separate the dewaxing solvents from the lube oil (>300 Da). Exxon filed several patents concerning membrane development, basically describing the feasibility of several polymeric membrane material, such as CA,[293] PA[294] and especially PI.[295,296] Finally, cooperation with Grace led to the development of an alternative SRNF-based process to recover these solvents, using spiral-wound Grace-Davison PI membranes (Fig. 13).[287,288] By replacing the evaporation step with a SRNF-membrane, a 99% pure solvent mixture could be obtained at refrigeration temperature, which could be directly recycled to the chilled feed stream. It is worth noting that this selectivity at industrial scale was even higher than extrapolated from bench-scale trials.

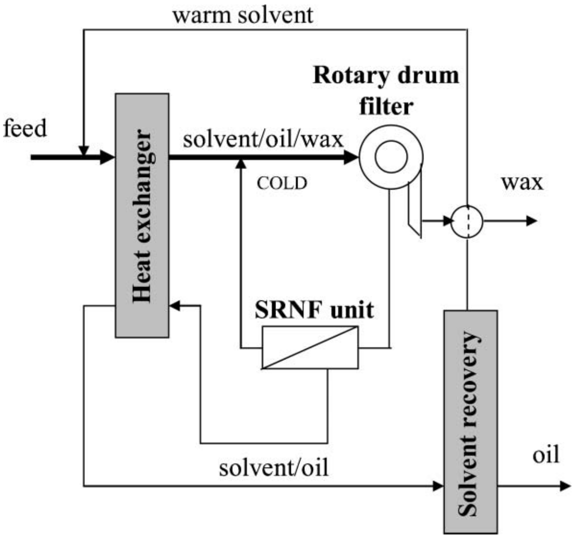


Fig. 13 Schematic representation of an SRNF-assisted lube oil dewaxing unit (adapted from ref. 287).

The capital investment for the SRNF was only 1/3 compared to the costs for the same capacity increase using conventional technologies. Moreover, the new process only needs 25% of the heat consumption, as well as 20% of the size and 10% of the refrigeration capacity,[192,287,288] resulting in a pay-back time of less than 1 year.[297] The anticipated membrane lifetime of 1.5 years has meanwhile been largely passed already, proving the long term stability of the polymeric membrane.[192]

Zhang and co-authors recently reported the synthesis of a novel SRNF-membrane, based on the PI 2,2-bis(2,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), to recover chilled MEK/toluene from lube oil filtrates. With permeabilities around 0.4 l (m^2 h bar)$^{-1}$ and oil rejections of 96%, the authors claimed to be competitive with the Grace-Davison PI membranes used in the Max-Dewax™ process [CF-S-continuous].[298]

For a very similar dewaxing process, excluding any secondary, non-membrane, recovery step, Shell patented already in 1987 the use of a solvent-cast membrane consisting of a 5 μm thick fluorinated silicone top-layer on a PP support.[116] Standard silicones would swell excessively under these conditions, but the introduction of fluorine in the structure allowed restriction of swelling in the toluene/MEK hydrocarbon mixture while preserving some selectivity[CU]. Later on, Shell also issued a patent covering the very general purification of hydrocarbon streams from solutes with a MW above 1000 and concentrations below 5 wt%. The process was exemplified with a dicyclopentadiene product stream being purified from its polyisoprene impurities using a PDMS/PEI membrane.[299]

In a Texaco-patent, thermally cross-linked poly(aliphatic terpene)/PAN composite membranes were claimed to be useful for similar separations of lube oil from MEK/toluene mixtures with an 87.2% rejection [CU],[136] which is significantly lower than the rejection obtained in the aforementioned studies. With a similar poly(1,3-butadiene)/PAN composite membranes, lube oil rejection was even lower still [CU].[300]

5.4.3 Applications with aromatics-containing refinery streams. In the eighties, Exxon-Mobil studied SRNF-applications extensively, even though it is not clear whether any of the patented processes has actually been implemented. Using a PI membrane in the alkylation of toluene with olefins over a heterogeneous catalyst, the alkylaromatics were recovered from the excess of toluene *via* SRNF. Even among the alkylaromatics, the membrane differentiated between the 'small' and the 'larger' reaction products.[301] A similar PI membrane, as well as a CA-based RO-membrane, was applied in the upgrading of a low-value middle distillate stream from a cracker by removing the majority of its aromatic content [CU].[302] However, more than one membrane separation stage was required to reach the set quality targets, while fluxes were generally too low as well.[302] The improved PI membranes claimed later, with a special emphasis on membrane conditioning, gave flux/selectivity combinations that were said to be sufficient for commercial applications.[303]

High-boiling polar aprotic solvents like NMP and DMF, are also used to extract the aromatic fraction from the middle distillate. Exxon researchers prepared a stable, interfacially-polymerized PA membrane and suggested to use this membrane to separate the aromatics from the extraction solvents. The synthesis of this membrane involved interfacial polymerization of PEI and a diisocyanate on a nylon support. The same membrane was also recommended for the separation of dewaxing solvents from lube oil filtrates.[304]

Shell patented a process to separate a fluid mixture containing hydrocarbon oil and an organic solvent, typically furfural, used in the extraction of aromatics from high-vacuum distillates, with a silicone-based membrane. The latter is substantially impermeable to the solvent, while the hydrocarbon oil is concentrated in the permeate stream.[305]

Methylstyrene has been purified from its dimeric form (present in a 5 wt% concentration) to a >99% pure monomer from a toluene solution using Starmem™ 120. The yield was found to be better than with alternative chromatography and realized at a much lower cost [CU].[306]

The potential of SRNF in aromatics enrichment of refinery streams has recently been assessed by Grace researchers.[5] Typical examples of such processes include aromatic isomerisations, hydrogenations, disproportionations and alkylations. With the selective permeation of aromatic hydrocarbons from a mixture of non-aromatic hydrocarbons,[223] SRNF would replace existing liquid/liquid extraction processes, hence lowering investment and energy costs. The retentate stream could be fed into a hydrocarbon separation or conversion process to be run at increased efficiency.

Insertion of a membrane separation into the purge stream of a toluene disproportionation unit, catalytically converting toluene to higher value products *p*-xylene and benzene, has shown that SRNF might be the preferred process. The process, schematically shown in Fig. 14, includes the separation equipment for removal of benzene and *p*-xylene, and the toluene-rich recycle loop providing multiple passes over the catalyst bed, thus allowing increased conversions of toluene. A fraction of the toluene recycle stream is sent to purge, in order to stop the build-up of undesirable non-aromatic hydrocarbons. With aromatics-selective SRNF-membranes, *i.e.* developmental Starmem™ varieties, a large fraction of the toluene present in the purge stream could be returned to the main reactor loop, while the concentrated non-aromatic impurities were sent for blending in the gasoline pool. Extended (over 200 h) continuous tests with commercial-scale spiral-wound SRNF-modules at 55 bar, subjected to hot (50 °C) aromatic feedstock, showed steady-state performance after an initial compaction period. Observed membrane selectivities were relatively low (up to 48%) but acceptable, since the SRNF-process only aims at reducing the downstream processing cost. An economic analysis suggested a payback period for the capital expenditure of only a few months [CF-L-continuous].[5]

The same authors suggested a similar SRNF-based aromatic enrichment in combination with distillation. An aromatics-selective SRNF-membrane would divert the desired aromatics around the distillation column that further purify the non-aromatics. This would increase the throughput to the column and improve the quality of the obtained aromatic product.[5]

5.4.4 Desulfurization of gasoline. Apart from solvent recovery in lube oil dewaxing and the removal of aromatics from hydrocarbon mixtures, Grace has also been investigating the feasibility of SRNF-membranes in another process with a potentially huge application scale in petrochemistry, *i.e.* the desulfurization of gasoline.[192,307] Due to environmental concerns, sulfur levels allowed in gasoline are being more and more restricted, *e.g.* to less than 50 ppm in the EU from 2005 onwards. Moreover, sulfur containing compounds might poison automotive exhaust catalysts. Increasing the capacity of existing hydrotreating installations would be an obvious choice to reduce S-contents, but it would involve a substantial capital expenditure, increased operating costs and a lowered gasoline octane number. Hydrogenation impacts octane levels by converting olefins to saturated hydrocarbons, which have lower octane contribution. This process is another example where a membrane separation can be integrated with other process units to improve the performance of the process as a whole, in this case by bypassing a large fraction of the feed around the hydrotreating unit. PI, polyurea-urethane and polysiloxane membranes have been tested in this respect to remove sulfur-containing hydrocarbon molecules from

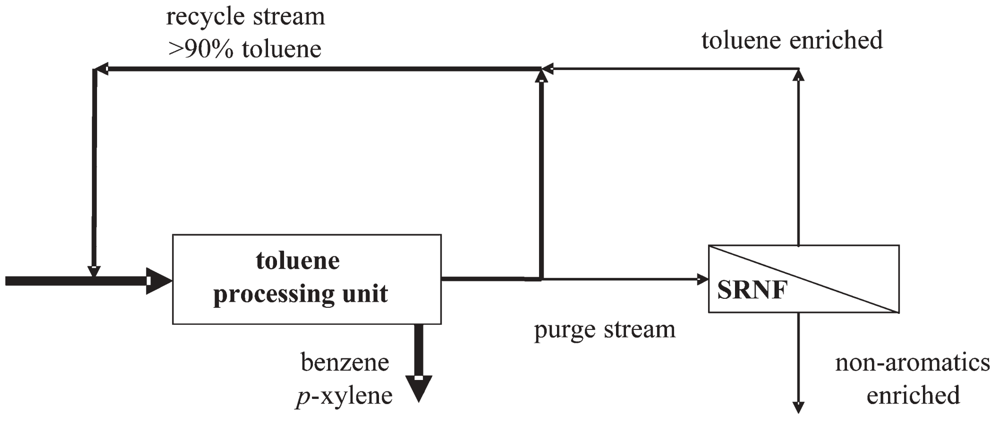


Fig. 14 Insertion of SRNF into the purge stream for toluene disproportionation (adapted from ref. 5).

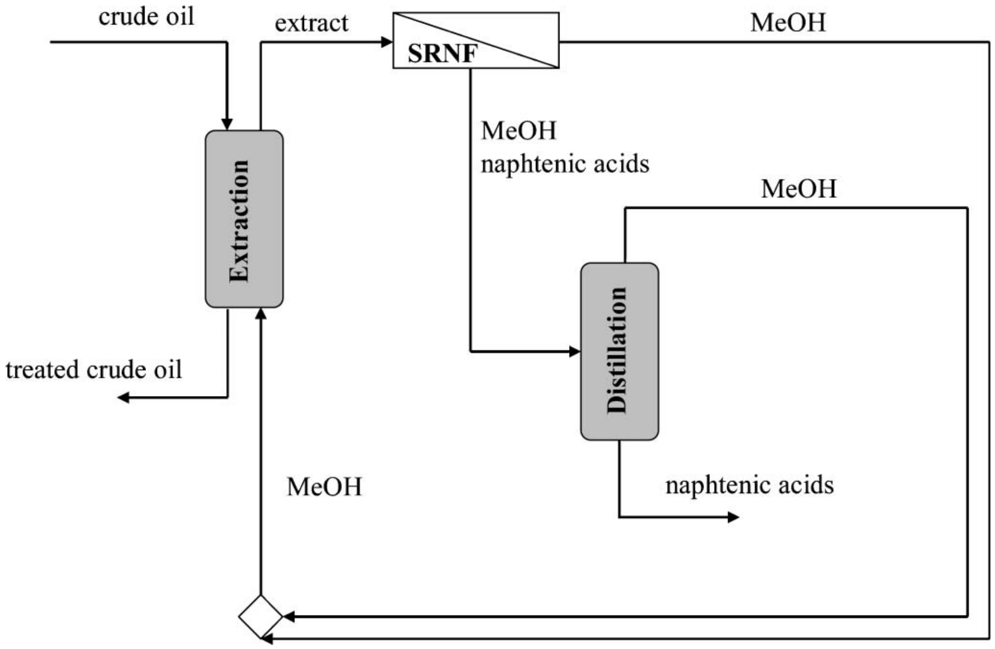


Fig. 15 Process scheme for crude oil deacidification (adapted from ref 297).

fluidized catalytic cracking (FCC) and other naptha streams, yielding clean consumer fuels.[307] The membranes are preferably used in PV mode (commercialized as S-Brane™), but in some cases the higher throughput and lower cost of SRNF outweighs the higher selectivities in PV.[192] The S-enriched permeate can be sent to the existing hydrodesulfurization unit, while the sulfur-deficient retentate fraction which maintains its octane value, is directly useful in the gasoline pool. Again, only very modest membrane selectivities seem to be expected from such process.[193,307]

5.4.5 Deacidification of crude oil. Crude oil may contain traces of organic acids, *e.g.* naphthenic acid. These impurities can cause corrosion problems, and are generally removed by extraction with polar solvents, *e.g.* methanol. After separation of the extract phase from the crude oil system, the polar solvent is recovered by distillation. BP patented an alternative process using SRNF, recovering the extraction solvent in the permeate while retaining the acid and/or its neutralization salts in the retentate (Fig. 15).[297,308] The patent suggests the use of Koch MPF membranes for this application, as well as Osmonics Desal membranes [CU].[297,308]

5.5 Pharmaceutical applications

5.5.1 Introduction. The following SRNF-applications have mostly been described in a pharmaceutical context, but could in fact just as well be combined with any organic synthesis of fine chemicals or intermediates. SRNF-membranes can be applied in drug synthesis between reaction steps or in the downstream processing. In case of thermolabile compounds, SRNF has an additional benefit compared to conventional thermal unit operations such as distillation. SRNF can be used to either retain a larger target molecule, or allow the target molecule to permeate while retaining the impurity.

5.5.2 Isolation and concentration of pharmaceuticals. An evident application is the isolation and concentration of antibiotics, pharmaceutical intermediates or peptides from organic solvents or aqueous solutions containing organic solvents. A particular example is the post-synthesis recovery of 6-aminopenicillanic acid (6-Apa, 216 Da), an intermediate in the enzymatic manufacturing of synthetic penicillin, from its bioconversion solution (Fig. 16)[297,309] with a MPS-44 membrane (Koch). With a recovery of 90–95%, product loss was restricted to a minimum, leading to a pay-back time of less than one year [CF-S].[297,309]

A PI-based SRNF-membrane has been developed for the concentration of the antibiotic spiramycin, forming a mixture of three compounds with MWs between 830 and 800 Da.[310] Spiramycin is extracted from bacterial broths with butyl acetate, which is traditionally recovered *via* evaporation. In addition to the energy consumption, this has also a negative influence on the quality of the final product. The membrane showed a stable long-term (35 days) separation performance with excellent solvent resistance and rejections around 99% [CF-L-continuous].[310]

5.5.3 Microfluidic purification. A Starmem™ 122 membrane has recently been fully integrated into a polyethylene terephthalate microfluidic format *via* transmission laser welding. The microfluidic set-up was limited to pressures of just 1.4 bar. At this pressure, methanol permeabilities up to 16 l $(m^2\ h\ bar)^{-1}$ were observed, considerably exceeding the literature-reported permeability values for Starmem™ 122.[311]

5.5.4 Solvent exchange. Synthesis of pharmaceuticals often involves multi-step reactions, each of which must be performed in another solvent, while the isolation of the product itself also occurs in a specific solvent. Solvent exchange is thus a key unit-operation in most sequential synthesis pathways to

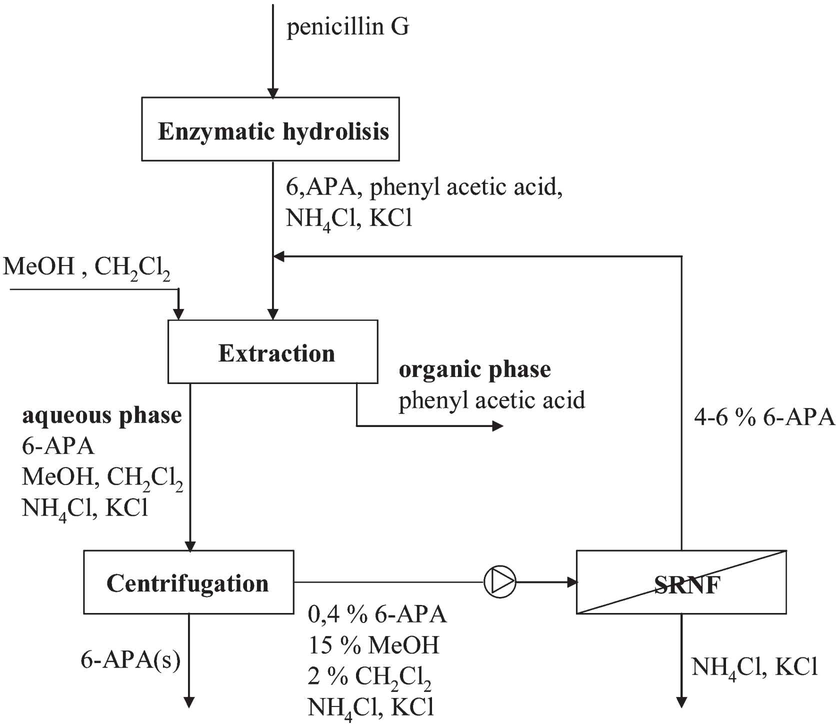


Fig. 16 Recovery of 6-APA from mother liquor with SRNF (adapted from ref. 297).

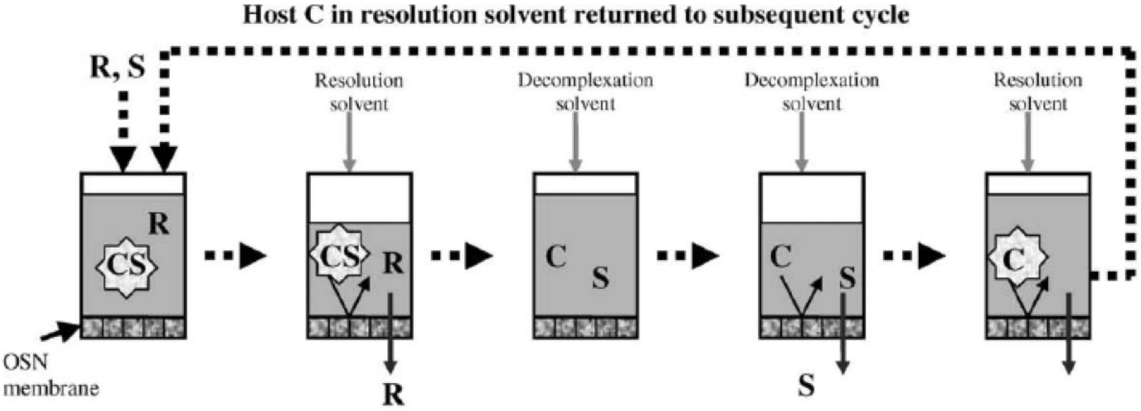


Fig. 17 Schematic representation of SRNF-combined enantioselective inclusion-complexation (taken from ref. 189). *R* and *S* = both enantiomers; C = complex.

concentrate active pharmaceutical intermediates, but at the same time also one of the major solvent-consuming processes in pharmaceuticals manufacturing.[197]

SRNF-based solvent exchanges have been suggested as an interesting alternative to swap target compounds from a high-boiling solvent to a lower-boiling solvent, or for solvent mixtures forming an azeotrope, *i.e.* for cases where distillation is no option. Such membrane-based solvent exchanges can take place at room temperature or at the operation temperature, irrespective the boiling point of the solvents involved. The latter is particularly useful for thermally labile compounds. The advantages of single-stage SRNF-based solvent exchange have been exemplified for TOABr, a PTC swapped from toluene to methanol,[15] and for erythromycin exchanged from methanol to EA.[167] The studied MPF[167] and Starmem™ membranes[15] did not show any solvent selectivity, thus allowing the solvent mixture and the low MW impurities to permeate simultaneously. The solvent exchange was described in both a continuous and a discontinuous diafiltration mode, in which intermediate solvent mixtures can possibly be reused in a following solvent exchange.[167,312] Membrane Extraction Technology commercialises this solvent exchange technology as MEMSOLVEX.[280]

5.5.5 Chiral separations. Chiral separations have also been coupled to SRNF. One approach, *i.e.* SRNF-combined enantioselective inclusion-complexation, based on the use of underivatised chiral hosts, uses high operating concentrations and is operated at ambient temperature (Fig. 14). In a first step, the chiral host and the racemate, *i.c.* (*R*,*R*)-TADDOL and 1-phenylethanol respectively, are mixed in the resolution solvent (hexane). The host complexes one enantiomer and leaves the solvent enriched in the uncomplexed form of the other enantiomer. The latter is much smaller and will thus preferably permeate through a SRNF-membrane (Starmem™ 122) with MWCO between the MWs of the host and the racemate. To recover all uncomplexed enantiomer, more resolution solvent is added and the solution is filtered again. A decomplexation solvent (toluene) is then added leading to the dissociation of the complex and allowing permeation of the complexed enantiomer. The decomplexation solvent is then removed by diafiltration with the resolution solvent. This approach offers an alternative to distillation-combined enantioselective inclusion complexes and opens up the chiral separation to non-volatile compounds and large-scale applications.[189] Related diastereomeric resolutions of chiral bases by organic acid resolving agents have also been shown to benefit from recycling of the resolving agent (di-*p*-toluoyl-L-tartaric acid) by SRNF.[188]

5.5.6 Solvent extractions. Another potential SRNF-application in the pharmaceutical sector is membrane-based solvent back extraction (MSBE), used to regenerate contaminated organic solvents following membrane-based solvent extraction (MSE). In MSE/MSBE, the overall solute mass transfer rate is controlled by the boundary layer resistances on both sides of the membrane and the resistance of the membrane itself. These resistances can be reduced by preferably filling the membrane pores with the phase preferred by the solute, which is for MSBE preferably the aqueous phase. Hydrophobic membrane pores can be exclusively filled with the organic phase and are advantageous only for MSE. Porous hydrophilic membranes on the other hand, can be filled either with the organic or with the aqueous phase, and are thus potentially useful for both MSE and MSBE. However, almost no hydrophilic solvent resistant membranes are available having the required pore sizes to provide stable aqueous-organic interfaces at higher organic phase pressures.[313]

In an attempt to synthesize a hydrophilic SRNF-membrane useful for MSBE, with optimized pore size and appropriate chemical resistance, Kosaraju and Sirkar coated the inner wall of hydrophilic porous Nylon-6 hollow fibers with an insolubilized hydrophobic PEI skin-layer. With this PEi/Nylon-6 composite membrane, both the restricted breakthrough pressure typically observed with microporous membranes, and the drastically reduced overall mass transfer coefficients when using dense SRNF-membranes could be overcome. MSBE of acetic acid from methyl isobutyl ketone (MIBK) into water, and phenol from MIBK into caustic solutions were used as model systems.[313]

5.5.7 Concentration of pharmaceuticals and solvent recovery in preparative HPLC. Another pharmaceutical application, described by Koch Membrane Systems is the recovery of solvents used in preparative HPLC.[314] SRNF can be applied in both concentrating the pharmaceutical compound in the product stream, and in purifying the solvent of the waste stream back to HPLC grade to enable re-use. Similarly, Kiryat Weitzman patented a multistage membrane system to process solvent streams containing biologically active compounds, generated in chromatographic separations.[315]

5.6 Fundamental mechanistic studies

Apart from the industrially relevant applications, SRNF also offers interesting new possibilities to study some more fundamental phenomena in organic chemistry. The mechanism of diastereomeric salt formation, observed earlier *via* different methods, was confirmed in an elegant way by using SRNF on a racemic mixture in the presence of a resolving agent.[190] Upon filtration, no diastereomer could be retained by the Starmem™ 122 membrane, even though the membrane MWCO in methanol would have allowed its full rejection. As crystallization did yield the diastereomeric salt, it could be concluded that there is no preferential binding of the resolving agent to the enantiomers in solution, but that racemic resolution can only be achieved *via* crystallization.

6 Upscaling and module design

Apart from the actual membrane, the design of a membrane plant also involves the modules (the smallest operational assembly into which membranes are packed), the membrane system (referring to the arrangement of the modules, pumps, piping, tanks, control and monitoring units, pretreatment and cleaning facilities) and the operating concept (batch, continuous or diafiltration). The module is the membrane 'housing' which simultaneously supports the membrane and provides effective fluid management.[2,316]

Membranes can be produced in flat sheet or cylindrical shape and this configuration determines the module geometry. Plate-and-frame and spiral-wound modules involve flat membranes, whereas tubular, capillary and hollow fiber modules are based on cylindrical membrane configurations (Fig. 18) with following dimensions: tubular (>10 mm diameter), capillary (0.5–10 mm) and hollow fiber (<0.5 mm). Some important aspects to be considered include the packing density, energy usage, fluid management and fouling control, ease of operation, compactness of the system, ease of manufacture, ease of cleaning and maintenance, and membrane replacement. Adequate pressure resistance and polarization control are particularly important for NF, while the chemical durability of the available module components should obviously also be guaranteed for applications in organic solvents.[2,316]

Plate-and-frame modules use flat sheet membranes. Sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other (Fig. 18a/b). The flow channels are usually thin (1 to 3 mm) and mostly filled with a mesh-like channel spacer. Plate-and-frame modules only provide a modest surface per volume characteristic (100–400 m^2 per m^3) and membrane replacement is possible, but labour-intensive. These modules are useful for small- to medium-scale applications in niche areas.[2,316]

The spiral-wound module design, which has a dominant position in industrial-scale NF-applications, basically consists of flat sheets wound around a central collection pipe (Fig. 18c/d). The membranes are glued along three sides to form 'leaves' attached to the permeate channel along the

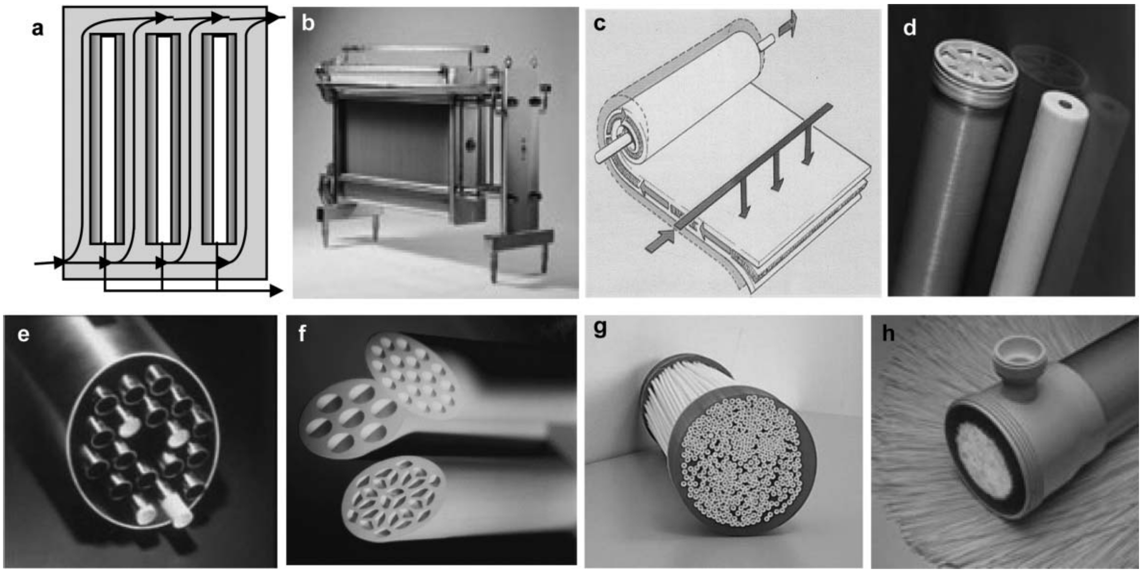


Fig. 18 Available membrane modules. (a) Scheme of plate-and-frame module, (b) plate-and-frame module, (c) scheme of spiral-wound module, (d) spiral-wound module, (e) tubular membranes, (f) monoliths, (g), capillary membranes, (h) hollow fibres (taken from ref. 317).

unsealed edge of the leaf. The internal side of the leaves contains a permeate spacer which is designed to avoid collapse upon filtration and conducts the permeate to the permeation tube. A feed channel spacer separates the top-layers of two flat sheet membranes. Pressurised feed flows axially, parallel to the permeation channel, through the thin spacer-filled channels between the membrane leaves, whereas the permeate flows radially through the spiral-wound permeate spacer towards the central collection pipe. The packing density of this module (300–1000 m^2 per m^3) is superior to plate-and-frame modules but depends much on the channel height, determined by the permeate and feed channel spacers. The spacers are particularly important as they promote shear at the membrane surface and thus determine the mass transfer and pressure drop characteristics of the module. The axial pressure drop over the leaf length due to the feed channel spacer, is accompanied by a radial pressure drop over the leaf width due to the permeate spacer. Several spiral-wound modules are usually assembled in one pressure vessel and connected in series *via* the central permeate tube.[2,316]

Tubular membranes have the active membrane surface at the inside of the tubes (Fig. 18e). In contrast to capillaries and hollow fibers, tubular membranes are generally not self-supporting, *i.e.* the walls are not strong enough to withstand collapse or bursting. Therefore, such membranes are placed inside a porous stainless steel, ceramic or plastic tube with the diameter of the tube generally being more than 10 mm. The feed solution always flows through the centre of the tubes. The packing density of tubular membranes is rather low (less than 300 m^2 per m^3). Monoliths (Fig. 18f) are a special type of ceramic tubular modules, where several tubes are introduced in a porous ceramic 'block', *e.g.* α-Al_2O_3. The inner surfaces of these tubes are then covered with the thin top-layer.[2,316]

Capillary modules (Fig. 18g) and hollow fibres (Fig. 18h) use membranes that are self-supporting. The difference between capillary and hollow fiber module is just a matter of dimensions since the module concept is the same. Hollow fiber modules contain thousands of fibres arranged in a 'bundle' with an epoxy outer shell around. Two types of module arrangement can be distinguished: 'inside-out' and 'outside-in' where respectively feed or permeate solution passes through the lumen of the capillaries and the other stream is collected on the outside.[2,316]

Especially for solvent separations, a functional module is critical to the successful continuous and long-term operation of a membrane system. All module elements (spacers, sealings, adhesives, *etc.*) as well as the membrane itself and the complete separation unit should meet the stability criteria – chemically, thermally and mechanically – imposed by the application. For refinery applications in particular, the chemical and thermal stability of the module components in hot hydrocarbon streams should be considered as well as the mechanical stability of the module assembly under high pressures.[5,192,318]

The development of a robust industrial membrane process involves moving from lab-scale coupon-tests, *via* larger stage-cut experiments and pilot plant tests, to a demo plant at the site and ultimately large-scale commercialization. Each step brings an increase in membrane area requirement, equipment, quantity of required feedstocks, execution time, analytical facilities (monitoring), technical issues and operating personnel.[192] Process development also requires the selection of an adequate operating concept, often dependent on the composition of the feed stream and the required product quality.

7 Concluding remarks and future prospects

SRNF is a relatively new separation technique with a large growth potential. Being an energy- and waste-efficient separation technique, current rising energy prizes and growing environmental concerns can only speed up further industrial implementation. Among others, the year-long trouble-free operation of Exxon-Mobil's large-scale SRNF-based Max-Dewax™ plant will undoubtedly be an inspiring example.

Notwithstanding some successes realized already, SRNF is still trying to find its place in academic research and for sure in industrial applications. The hesitation from process engineers and managers to switch from conventional, well-established separation methods to membrane separations, combined with the current focus of membrane companies on the more lucrative aqueous applications, currently hampers new industrial developments. Most probably, SRNF will first be implemented to de-bottleneck, complement or upgrade existing production facilities, rather then substitute them. Many of the potential applications, *e.g.* in the oleo- or petrochemistry are of such a huge scale, hence so capital-intensive, that switching the current process to SRNF is not obvious for installations that still do the job well enough, even if well-performing membranes would be available, and economical or environmental profits could be made. In some cases, SRNF as such will not be capable to completely isolate the product or catalyst from its medium, but only to concentrate it. Further purification or isolation can then take place with other conventional separation techniques at considerably increased efficiencies, thanks to the membrane pre-treatment. For applications allowing only low thermal stress or using non-volatile solvents however, membrane technology can practically be the only alternative to de-bottleneck the process.

Parallel to these initiatives at process level, there is still a task for material and membrane scientists to develop new SRNF membranes with improved performance. Many scientifically interesting, technically challenging and commercially attractive separation problems in organic solvents cannot be solved with the currently available SRNF-membranes. Many more processes could be realized if stable membranes with high selectivities, competitive flux and sufficient long-term stability would be available. Truly molecule-selective separations require novel functional high-performance membranes with high selectivities, *e.g.* for isomers, enantiomers or biomolecules. Overcoming the trade-off between selectivity and permeability is another important issue hampers further developments.

The different requirements discussed above can be efficiently addressed by various approaches within the field of nanotechnology. Functional polymeric membranes offer a large potential.[319] These membranes are often based on tailored functional macromolecular architectures instead of just bulk polymer properties. Advanced polymer processing, tailored polymer synthesis for subsequent membrane manufacturing and surface functionalization are some of the routes towards functional polymeric membranes. Segmented polymer networks,[320] interpenetrating networks[321] and multilayer polyelectrolyte membranes[322] are just some of the advanced polymer structures with potential for SRNF. Mixed-matrix membranes, combining the advantages of both polymeric and ceramic membranes, also have potential for SRNF. Some important industrial solvents, such as THF, DMF, DMSO, NMP and DCM, are still critical for most currently available SRNF-membranes. Aprotic solvents especially are demanding and require an extremely high chemical stability from the whole membrane system. (Modified) ceramics can be an option here, even though not a single ceramic has the potential to be suited for all different solvents. Moreover, ceramic membranes will remain more expensive and suffer from brittleness and a low surface/volume ratio when constructed in a module. Their use might thus basically remain limited to small-scale, high-value separations. In addition to solvent stability, improved base and acid stability of SRNF-membranes needs attention as well. By preference, the thermal and pressure resistance of the membranes should also match the conditions of the processes in which they are introduced, thus preventing expensive cooling/heating and pressurization/depressurization cycles. Compaction resistance and membrane attack under reactive conditions can thus be critical issues. Another aspect that needs further improvement is the ‘steepness’ of the MWCO-curve as it is of importance to realize a ‘clear cut’ between full rejection of one solute and full permeation of another. With truly sharp MWCO-curves below 300 Da, the large potential of solvent separations could come in reach. New cutting edge developments in material science might still be far from large-scale production, but can on the longer term also bring solutions to these problems.[323,324] Finally, membrane pre-conditioning needs sufficient attention, no matter which membrane material is being used.

The advent of more advanced, better performing and well-characterized membranes can only accelerate the substitution of existing unit operations by SRNF. With the recent introduction of high throughput membrane synthesis and screening, coupled to advanced experimental design, extremely well-performing tailor-made membranes might be obtained.[32,33] Especially for large-scale industrial processes, the lab-scale development of such tailor-made membranes with subsequent upscaling to production scale, might be a worthwhile and economic option. It would only further broaden the portfolio of commercially available SRNF-membranes, thus probably decreasing prices and covering more potential applications.

For catalytic applications, the membrane requirements mentioned above are also valid, but some specific challenges remain on the catalysis level as well. Catalyst stability throughout the complete reaction cycle is a key factor in the success of the SRNF-coupled catalysis approach. Potential accumulation of side-products at the retentate side, could be another problem, in the first instance to be solved by development of more selective catalysts.

SRNF is currently still largely ignored as a potential lab-scale technique for day-by-day use to facilitate multi-step organic syntheses involving solvent-intensive column purifications, salting-out steps, batch adsorption, crystallization, *etc.* A clear catalogue-like set of SRNF-membranes with indication of solvent compatibility would be helpful here, ideally supplemented with a solvent dependent MWCO (which would still be not more than a rough indication, as molecular shape and charge of the solute would still influence separation). Availability of a small-volume SRNF bench-scale test-cell would already be a first help for the synthesizing organic chemist, who is often still unaware of SRNF as a separation technique. If the synthesis processes thus developed at lab-scale were to be upscaled, the implementation of SRNF as an essential step in the actual industrial process would become much more obvious.

On the level of membrane transport modeling, the gap is still too wide between pure ‘black’ or even ‘grey’ box mathematical modeling and thorough physico-chemical characterization to verify interpretations of the calculated values. The use of high-resolution characterization techniques might be needed here to go down to the atomic scale at which SRNF takes place. Obviously, any further development of models predicting membrane performance with input of only some basic feed and membrane characteristics would be more than welcome.

As a young technology still exploring and expanding its limits, it is logical that future focus still needs and surely will be shifted towards more technical-operational aspects, like mass transfer limitations in feed solution (concentration polarization, fouling, *etc.*), membrane compaction, upscaling issues, long term membrane and module reliability, module and plant design.

References

1 R. J. Petersen, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, foreword, pp. xx–xxi.
2 M. Mulder, in *Basic Principles of Membrane Technology*, ed. M. Mulder, Kluwer Academic Publishers, Dordrecht, 2nd edn., 2004, ch. 3, pp. 71–156.
3 W. J. Koros, Y. H. Ma and T. Shimidzu, *J. Membr. Sci.*, 1996, **120**, 149.
4 S. Loeb, *Science*, 1965, **147**, 1241.
5 L. S. White and C. R. Wildemuth, *Ind. Eng. Chem. Res.*, 2006, **45**, 9136.
6 D. F. Stamatialis, N. Stafie, K. Buadu, M. Hempenius and M. Wessling, *Proceedings of the International Workshop on Membranes in Solvent Filtration*, Leuven, Belgium, 2006.
7 N. Stafie, D. F. Stamatialis and M. Wessling, *Sep. Purif. Technol.*, 2005, **45**, 220.
8 N. Stafie, D. F. Stamatialis and M. Wessling, *J. Membr. Sci.*, 2004, **228**, 103.
9 H. J. Zwijnenberg, M. Boerrigter, G. H. Koops and M. Wessling, Proceedings of the International Conference on Membranes and Membrane Processes (ICOM), Providence (RI), USA, 2005.
10 J. Kwiatkowski and M. Cheryan, *Sep. Sci. Technol.*, 2005, **40**, 2651.
11 T. Tsuru, T. Sudoh, T. Yoshioka and M. Asaeda, *J. Membr. Sci.*, 2001, **185**, 253.
12 L. E. M. Gevers, G. Meyen, K. De Smet, P. Van De Velde, F. Du Prez, I. F. J. Vankelecom and P. A. Jacobs, *J. Membr. Sci.*, 2006, **274**, 173.
13 Y. H. See Toh, X. X. Loh, K. Li, A. Bismarck and A. G. Livingston, *J. Membr. Sci.*, 2007, **291**, 120.
14 A. I. Schäfer, N. Andritsos, A. J. Karabelas, E. M. V. Hoek, R. Schneider and M. Nyström, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, ch. 8, pp. 169–240.
15 A. Livingston, L. Peeva, S. Han, D. Nair, S. S. Luthra, L. S. White and L. M. Freitas dos Santos, *Ann. N. Y. Acad. Sci.*, 2003, **984**, 123.
16 D. F. Stamatialis, N. Stafie, K. Buadu, M. Hempenius and M. Wessling, *J. Membr. Sci.*, 2006, **279**, 424.
17 P. Silva and A. G. Livingston, *J. Membr. Sci.*, 2006, **280**, 889.
18 P. Silva and A. G. Livingston, *Desalination*, 2006, **199**, 248.
19 L. G. Peeva, E. Gibbins, S. S. Luthra, L. S. White, R. P. Stateva and A. G. Livingston, *J. Membr. Sci.*, 2004, **236**, 121.
20 I. F. J. Vankelecom, K. De Smet, L. E. M. Gevers, A. G. Livingston, S. Aerts, S. Kuypers and P. A. Jacobs, *J. Membr. Sci.*, 2004, **231**, 99.
21 E. Gibbins, M. D'Antonio, D. Nair, L. S. White, L. M. Freitas dos Santos, I. F. J. Vankelecom and A. G. Livingston, *Desalination*, 2002, **147**, 307.
22 Y. Zhao and Q. Yuan, *J. Membr. Sci.*, 2006, **280**, 195.
23 Y. H. See-Toh, F. C. Ferreira and A. G. Livingston, *J. Membr. Sci.*, 2007, **299**, 236.
24 L. E. M. Gevers, S. Aldea, I. F. J. Vankelecom and P. A. Jacobs, *J. Membr. Sci.*, 2006, **281**, 741.
25 U. Razdan, S. V. Joshi and V. J. Shah, *Curr. Sci.*, 2003, **85**, 761.
26 *US Pat.*, 5 265 734, 1993.
27 E. M. Tsui and M. Cheryan, *J. Membr. Sci.*, 2004, **237**, 61.
28 S. Loeb and S. Sourirajan, *Adv. Chem. Ser.*, 1963, **38**, 117.
29 I. F. J. Vankelecom and L. E. M. Gevers, in *Green Separation Processes. Fundamentals and Applications*, ed. C. A. M. Alfonso and J. G. Crespo, Wiley-VCH, Weinheim, 2005, ch. 3.6, pp. 251–270.
30 R. J. Petersen, *J. Membr. Sci.*, 1993, **83**, 81.
31 I. F. J. Vankelecom, K. De Smet, L. E. M. Gevers and P. A. Jacobs, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, ch. 3, pp. 33–65.
32 M. Bulut, L. E. M. Gevers, J. S. Paul, I. F. J. Vankelecom and P. A. Jacobs, *J. Comb. Sci.*, 2006, **8**, 168.
33 P. Vandezande, L. E. M. Gevers, J. S. Paul, I. F. J. Vankelecom and P. A. Jacobs, *J. Membr. Sci.*, 2005, **250**, 305.
34 P. R. Buch, D. J. Mohan and A. V. R. Reddy, *Polym. Int.*, 2006, **55**, 391.
35 N. Oh, J. Jegal and K. Lee, *J. Appl. Polym. Sci.*, 2001, **80**, 2729.
36 X. Lu, X. Bian and L. Shi, *J. Membr. Sci.*, 2002, **210**, 3.
37 H. I. Kim and S. S. Kim, *J. Membr. Sci.*, 2006, **286**, 193.
38 A. P. Korikov, P. B. Kosaraju and K. K. Sirkar, *J. Membr. Sci.*, 2006, **279**, 588.
39 K. Ebert, J. Koll, M. F. J. Dijkstra and M. Eggers, *J. Membr. Sci.*, 2006, **285**, 75–85.
40 *US Pat.*, 6 986 844, 2006.
41 *Eur. Pat.*, EP0511900, 1992.
42 I. F. J. Vankelecom, B. Moermans, G. Verschueren and P. A. Jacobs, *J. Membr. Sci.*, 1999, **158**, 289.
43 S. P. Nunes and K. Peinemann, in *Membrane Technology in the Chemical Industry*, ed. S. P. Nunes and K. Peinemann, Wiley-VCH, Weinheim, 2006, part I, pp. 1–85.
44 S. A. McKelvey and W. J. Koros, *J. Membr. Sci.*, 1996, **112**, 29.
45 C. A. Smolders, A. J. Reuvers, R. M. Boom and I. M. Wienk, *J. Membr. Sci.*, 1992, **73**, 259.
46 A. F. Ismail and L. P. Yean, *J. Appl. Polym. Sci.*, 2003, **88**, 442.
47 E. P. Cuperus and K. Ebert, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, ch. 21, pp. 521–536.
48 N. Leblanc, D. Le Cerf, C. Chappey, D. Langevin, M. Métayer and G. Muller, *Sep. Purif. Technol.*, 2001, **22–23**, 277.
49 H. Yanagishita, T. Nakane and H. Yoshitome, *J. Membr. Sci.*, 1994, **89**, 215.
50 K. Boussu, C. Vandecasteele and B. Van der Bruggen, *Polymer*, 2006, **47**, 3464.
51 A. F. Ismail and P. Y. Lai, *Sep. Purif. Technol.*, 2003, **33**, 127.
52 I. Kim, H. Yoon and K. Lee, *J. Appl. Polym. Sci.*, 2002, **84**, 1300.
53 H. Hicke, I. Lehmann, G. Malsch, M. Ulbricht and M. Becker, *J. Membr. Sci.*, 2002, **198**, 187.
54 Y. Dai, X. Jian, S. Zhang and M. D. Guiver, *J. Membr. Sci.*, 2001, **188**, 195.
55 I. Pinnau and W. Koros, *J. Polym. Sci., Part B: Polym. Phys.*, 1993, **31**, 419.
56 Y. Yang, X. Jian, D. Yang, S. Zhang and L. Zou, *J. Membr. Sci.*, 2006, **270**, 1.
57 I. Kim, K. Lee and T. M. Tak, *J. Membr. Sci.*, 2001, **183**, 235.
58 J. Lai, F. Lin, C. Wang and D. Wang, *J. Membr. Sci.*, 1996, **118**, 49.
59 A. J. Reuvers and C. A. Smolders, *J. Membr. Sci.*, 1987, **34**, 259.
60 N. A. Mohamad, *Polymer*, 1997, **38**, 4705.
61 K. C. Gupta, *J. Appl. Polym. Sci.*, 1997, **66**, 643.
62 C. Dias, M. Rosa and M. de Pinho, *J. Membr. Sci.*, 1998, **138**, 259.
63 Q. Zheng, P. Wang and Y. Yang, *J. Membr. Sci.*, 2006, **279**, 230.
64 M. Han and S. Nam, *J. Membr. Sci.*, 2002, **202**, 55.
65 J. Kim and K. Lee, *J. Membr. Sci.*, 1998, **138**, 153.
66 A. F. Ismail and A. R. Hassan, *Sep. Purif. Technol.*, 2007, **55**, 98.
67 S. H. Yoo, J. H. Kim, J. Y. Jho, J. Won and Y. S. Kang, *J. Membr. Sci.*, 2004, **236**, 203.
68 B. Jung, J. K. Yoon, B. Kim and H. Rhee, *J. Membr. Sci.*, 2004, **243**, 45.
69 W. Bowen, T. Doneva and H. Yin, *J. Membr. Sci.*, 2001, **181**, 253.
70 I. Okazaki, H. Ohya, S. I. Semenova, M. Aihara and Y. Negishi, *J. Membr. Sci.*, 1998, **141**, 277.

71 D. Wang, F. Lin, T. Wu and J. Lai, *J. Membr. Sci.*, 1998, **142**, 191.
72 N. Leblanc, D. Le Cerf, C. Chappey, D. Langevin, M. Métayer and G. Muller, *J. Appl. Polym. Sci.*, 2003, **89**, 1838.
73 H. Ohya, I. Okazaki, M. Aihara, S. Tanisho and Y. Negishi, *J. Membr. Sci.*, 1997, **123**, 143.
74 F. G. Paulsen, S. S. Shojaie and W. B. Krantz, *J. Membr. Sci.*, 1994, **91**, 265.
75 X. Jian, Y. Dai, G. He and G. Chen, *J. Membr. Sci.*, 1999, **161**, 185.
76 S. P. Deshmukh and K. Li, *J. Membr. Sci.*, 1998, **150**, 81.
77 S. Konagaya, H. Kuzumoto and O. Watanabe, *J. Appl. Polym. Sci.*, 2001, **80**, 505.
78 K. Chun, S. Jang, H. Kim, Y. Kim, H. Han and Y. Joe, *J. Membr. Sci.*, 2000, **169**, 197.
79 A. Bottino, G. Capannelli and S. Munari, *J. Appl. Polym. Sci.*, 1985, **30**, 3009.
80 *US Pat.*, 6 180 008, 2001.
81 M. L. Yeow, Y. Liu and K. Li, *J. Membr. Sci.*, 2005, **258**, 16.
82 *US Pat.*, 5 725 769, 1998.
83 *US Pat.*, 5 032 282, 1991.
84 *US Pat.*, 5 039 421, 1991.
85 J. Wang, Z. Yue, J. S. Ince and J. Economy, *J. Membr. Sci.*, 2006, **286**, 333.
86 K. Peinemann, K. Ebert, H. Hicke and N. Scharnagl, *Environ. Prog.*, 2001, **20**, 17.
87 *Eur. Pat.*, WO9947247, 1999.
88 J. Chen, J. Li, Z. Zhao, D. Wang and C. Chen, *Surf. Coat. Technol.*, 2007, **201**, 6789.
89 J. E. Cadotte, *ACS Symp. Ser.*, 1985, **269**, 273.
90 C. K. Kim, J. H. Kim, I. J. Roh and J. J. Kim, *J. Membr. Sci.*, 2000, **165**, 189.
91 I. J. Roh, S. Y. Park, J. J. Kim and C. K. Kim, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 1821.
92 Z. Yhou, Y. Sanchuan, L. Meihong and G. Congjie, *J. Membr. Sci.*, 2006, **270**, 162.
93 M. M. Jayarani and S. S. Kulkarni, *Desalination*, 2000, **130**, 17.
94 S. Chen, D. Chang, R. Liou, C. Hsu and S. Lin, *J. Appl. Polym. Sci.*, 2002, **83**, 1112.
95 J. Jegal, S. Min and K. Lee, *J. Appl. Polym. Sci.*, 2002, **86**, 2781.
96 M. Hirose, H. Ito and Y. Kamiyama, *J. Membr. Sci.*, 1996, **121**, 209.
97 *US Pat.*, 5 274 047, 1993.
98 S. Verissimo, K. Peinemann and J. Bordado, *J. Membr. Sci.*, 2005, **264**, 48.
99 A. L. Ahmad and B. S. Ooi, *J. Membr. Sci.*, 2005, **255**, 67.
100 Y. Song, P. Sun, L. L. Henry and B. Sun, *J. Membr. Sci.*, 2005, **251**, 67.
101 *US Pat.*, 5 755 964, 1998.
102 *US Pat.*, 4 765 897, 1988.
103 A. P. Rao, N. V. Desai and R. Rangarajan, *J. Membr. Sci.*, 1997, **124**, 263.
104 S. S. Köseoglu, J. T. Lawhon and E. W. Lusas, *J. Am. Oil Chem. Soc.*, 1990, **67**, 315.
105 I. Kim, J. Jegal and K. Lee, *J. Polym. Sci., Part B: Polym. Phys.*, 2002, **40**, 2151.
106 I. Kim and K. Lee, *Ind. Eng. Chem. Res.*, 2002, **41**, 5523.
107 *US Pat.*, 6 887 380, 2005.
108 *US Pat.*, 5 173 191, 1992.
109 G. R. Daisley, M. G. Dastgir, F. C. Ferreira, L. G. Peeva and A. G. Livingston, *J. Membr. Sci.*, 2006, **268**, 20.
110 L. E. M. Gevers, I. F. J. Vankelecom and P. A. Jacobs, *J. Membr. Sci.*, 2006, **278**, 199.
111 *US Pat.*, 4 618 534, 1988.
112 *Eur. Pat.*, WO9267430, 1996.
113 *US Pat.*, 5 093 002, 1992.
114 S. Tarleton, J. P. Robinson, C. R. Millington and A. Niemeijer, *J. Membr. Sci.*, 2005, **252**, 123.
115 J. P. Robinson, E. S. Tarleton, K. Ebert, C. R. Millington and A. Niemeijer, *Ind. Eng. Chem. Res.*, 2005, **44**, 3238.
116 *US Pat.*, 4 748 288, 1988.
117 S. Aerts, A. Vanhulsel, A. Buekenhoudt, H. Weyten, S. Kuypers, H. Chen, M. Bryjak, L. E. M. Gevers, I. F. J. Vankelecom and P. A. Jacobs, *J. Membr. Sci.*, 2006, **275**, 212.
118 I. F. J. Vankelecom, E. Scheppers, R. Heus and J. B. Uytterhoeven, *J. Phys. Chem.*, 1994, **98**, 12390.
119 *Eur. Pat.*, EP1699546, 2006.
120 L. E. M. Gevers, I. F. J. Vankelecom and P. A. Jacobs, *Chem. Commun.*, 2005, **19**, 2500.
121 E. S. Tarleton, J. P. Robinson and M. Salman, *J. Membr. Sci.*, 2006, **280**, 442.
122 *US Pat.*, 5 024 765, 1991.
123 *Eur. Pat.*, EP0392982, 1990.
124 *US Pat.*, 5 151 182, 1992.
125 K. J. Kim, G. Chowdhury and T. Matsuura, *J. Membr. Sci.*, 2000, **179**, 43.
126 *US Pat.*, 4 753 725, 1988.
127 J. Jegal and K. Lee, *J. Appl. Polym. Sci.*, 1999, **72**, 1755.
128 K. Lang, S. Sourirajan, T. Matsuura and G. Chowdhury, *Desalination*, 1996, **104**, 185.
129 D. A. Musale and A. Kumar, *J. Appl. Polym. Sci.*, 2000, **77**, 1782.
130 A. Kumar and D. Musale, *Sep. Purif. Technol.*, 2000, **31**, 27.
131 *US Pat.*, 6 113 794, 2000.
132 K. Lee, M. Teng, H. Lee and J. Lai, *J. Membr. Sci.*, 2000, **164**, 13.
133 H. Ohya, M. Shibata, Y. Negishi, Q. Guo and H. Choi, *J. Membr. Sci.*, 1994, **90**, 91.
134 J. Huang, Q. Guo, H. Ohya and J. Fang, *J. Membr. Sci.*, 1998, **144**, 1.
135 *US Pat.*, 5 266 207, 1993.
136 *US Pat.*, 5 234 579, 1993.
137 A. V. Volkov, D. F. Stamatialis, V. S. Khotimsky, V. V. Volkov, M. Wessling and N. A. Platé, *J. Membr. Sci.*, 2006, **281**, 351.
138 E. Florian, M. Modesti and M. Ulbricht, *Ind. Eng. Chem. Res.*, 2007, **46**, 4891.
139 C. Guizard, J. Palmeri, P. Amblard, J. Diaz and J. Lasserre, Proceedings of the Fifth International Conference on Inorganic Membranes (ICIM), Nagoya, Japan, 1998.
140 L. Cot, A. Ayral, J. Durand, C. Guizard, N. Hovnanian, A. Julbe and A. Larbot, *Solid State Sci.*, 2000, **2**, 313.
141 R. S. A. de Lange, J. H. A. Hekkink, K. Keizer and A. J. Burggraaf, *J. Membr. Sci.*, 1995, **99**, 57.
142 T. Tsuru, T. Sudoh, S. Kawahara, T. Yoshioka and M. Asaeda, *J. Colloid Interface Sci.*, 2000, **228**, 292.
143 S. Condom, S. Chemlal, W. Chu, M. Persin and A. Larbot, *Sep. Purif. Technol.*, 2001, **25**, 545.
144 I. Voigt, P. Puhlfürβ and J. Töpfer, *Key Eng. Mater.*, 1997, **132–136**, 1735.
145 P. Puhlfürß, A. Voigt, R. Weber and M. Morbé, *J. Membr. Sci.*, 2000, **174**, 123.
146 R. Vacassy, C. Guizard, V. Thoraval and L. Cot, *J. Membr. Sci.*, 1997, **132**, 109.
147 I. Voigt, *Chem.-Ing.-Tech.*, 2005, **77**, 559.
148 S. Benfer, P. Árki and G. Tomandl, *Adv. Eng. Mat.*, 2004, **6**, 495.
149 http://www.inopor.de.
150 I. Voigt, M. Stahn, St. Wöhner, A. Junghans, J. Rost and W. Voigt, *Sep. Purif. Technol.*, 2001, **25**, 509.
151 A. Guizard, A. Ayral and A. Julbe, *Desalination*, 2002, **147**, 275.
152 T. Tsuru, S. Wada, S. Izumi and M. Asaeda, *J. Membr. Sci.*, 1998, **149**, 127.
153 T. Tsuru, M. Miyawaki, H. Kondo, T. Yoshioka and M. Asaeda, *Sep. Purif. Technol.*, 2003, **32**, 105.
154 T. Tsuru, S. Izumi, T. Yoshioka and M. Asaeda, *AIChE J.*, 2000, **46**, 565.
155 T. Tsuru, M. Miyawaki, T. Yoshiaka and M. Asaeda, *AIChE J.*, 2006, **52**, 522.
156 B. Verrecht, R. Leysen, A. Buekenhoudt, C. Vandecasteele and B. Van der Bruggen, *Desalination*, 2006, **200**, 385.
157 *Eur. Pat.*, EP1603663, 2004.
158 http://www.kochmembrane.com/.
159 J. Geens, A. Hillen, B. Bettens, B. Van der Bruggen and C. Vandecasteele, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1371.
160 D. R. Machado, D. Hasson and R. Semiat, *J. Membr. Sci.*, 2000, **166**, 63.
161 J. A. Whu, B. C. Baltzis and K. K. Sirkar, *J. Membr. Sci.*, 2000, **170**, 159.
162 B. Van der Bruggen, J. Geens and C. Vandecasteele, *Sep. Sci. Technol.*, 2002, **37**, 783.
163 X. J. Yang, A. G. Livingston and L. Freitas dos Santos, *J. Membr. Sci.*, 2001, **190**, 45.

164 J. T. Scarpello, D. Nair, L. M. Freitas dos Santos, L. S. White and A. G. Livingston, *J. Membr. Sci.*, 2002, **203**, 71.
165 S. S. Luthra, X. Yang, L. M. Freitas dos Santos, L. S. White and A. G. Livingston, *J. Membr. Sci.*, 2002, **201**, 65.
166 L. P. Raman, M. Cheryan and N. Rajagopolan, *J. Am. Oil Chem. Soc.*, 1996, **73**, 219.
167 J. P. Sheth, Y. Qin, K. K. Sirkar and B. C. Baltzis, *J. Membr. Sci.*, **211**, 251.
168 D. Bhanushali and D. Bhattacharyya, *Ann. N. Y. Acad. Sci.*, 2003, **984**, 159.
169 Y. Zhao and Q. Yuan, *J. Membr. Sci.*, 2006, **279**, 453.
170 J. Geens, B. Van der Bruggen and C. Vandecasteele, *Sep. Purif. Technol.*, 2006, **48**, 255.
171 J. Geens, K. Boussu, C. Vandecasteele and B. Van der Bruggen, *J. Membr. Sci.*, 2006, **281**, 139.
172 J. Geens, K. Peeters, B. Van der Bruggen and C. Vandecasteele, *J. Membr. Sci.*, 2005, **255**, 255.
173 P. Silva, S. Han and G. Livingston, *J. Membr. Sci.*, 2005, **262**, 49.
174 S. J. Han, S. S. Luthra, L. Peeva, X. J. Yang and A. G. Livingston, *Sep. Sci. Technol.*, 2003, **38**, 1899.
175 J. Geens, B. Van der Bruggen and C. Vandecasteele, *Chem. Eng. Sci.*, 2002, **57**, 2511.
176 B. Van der Bruggen, J. C. Jansen, A. Figoli, J. Geens, D. Van Baelen, E. Drioli and C. Vandecasteele, *J. Phys. Chem. B*, 2004, **108**, 13273.
177 M. Schmidt, S. Mirza, R. Schubert, H. Rödicker, S. Kattanek and J. Malisz, *Chem.-Ing.-Tech.*, 1999, **71**, 199.
178 D. Bhanushali, S. Kloos and D. Bhattacharyya, *J. Membr. Sci.*, 2002, **208**, 343.
179 http://www.membrane-extraction-technology.com/.
180 J. L. C. Santos, A. M. Hidalgo, R. Oliveira, S. Velizarov and J. G. Crespo, *J. Membr. Sci.*, 2007, 191–204.
181 H. T. Wong, Y. H. See-Toh, F. C. Ferreira, R. Crook and A. G. Livingston, *Chem. Commun.*, 2006, **19**, 2063.
182 H. Wong, C. J. Pink, F. C. Ferreira and A. G. Livingston, *Green Chem.*, 2006, **8**, 373.
183 D. Nair, J. T. Scarpello, I. F. J. Vankelecom, L. M. Freitas dos Santos, L. S. White, R. J. Kloetzing, T. Welto and A. G. Livingston, *Green Chem.*, 2002, **4**, 319.
184 D. Nair, S. S. Luthra, J. T. Scarpello, L. S. White, L. M. Freitas dos Santos and A. G. Livingston, *Desalination*, 2002, **147**, 301.
185 D. Nair, J. T. Scarpello, L. S. White, L. M. Freitas dos Santos, I. F. J. Vankelecom and A. G. Livingston, *Tetrahedron Lett.*, 2001, **42**, 8219.
186 S. S. Luthra, X. Yang, L. M. Freitas dos Santos, L. S. White and A. G. Livingston, *Chem. Commun.*, 2001, 1468.
187 C. Roengpithya, D. A. Patterson, P. C. Taylor and A. G. Livingston, *Desalination*, 2006, **199**, 195.
188 F. C. Ferreira, H. Macedo, U. Cocchini and A. G. Livingston, *Org. Process Res. Dev.*, 2006, **10**, 784.
189 N. F. Ghazali, F. C. Ferreira, A. J. P. White and A. G. Livingston, *Tetrahedron: Asymmetry*, 2006, **17**, 1846.
190 N. F. Ghazali, D. A. Patterson and A. G. Livingston, *Chem. Commun.*, 2004, **8**, 962.
191 S. Han, H. Wong and A. G. Livingston, *Chem. Eng. Res. Des.*, 2005, **83**, 309.
192 L. S. White, *J. Membr. Sci.*, 2006, **286**, 26.
193 J. C. Lin and A. G. Livingston, *Chem. Eng. Sci.*, 2007, **62**, 2728.
194 J. T. Rundel, B. K. Paul and V. T. Remcho, *J. Chromatogr., A*, 2007, DOI: 10.1016/j.chroma.2007.06.042.
195 R. Valadez-Blanco, F. C. Ferreira, R. F. Jorge and A. G. Livingston, *J. Membr. Sci.*, 2007, DOI: 10.1016/j.memsci.2007.04.032.
196 http://www.solsep.com/.
197 F. P. Cuperus, *Chem.-Ing.-Tech.*, 2005, **77**, 1000.
198 B. Van der Bruggen, J. C. Jansen, A. Figoli, J. Geens, K. Boussu and E. Drioli, *J. Phys. Chem. B*, 2006, **110**, 13799.
199 G. Bargeman, J. Albers, J. B. Westerlink, C. F. H. Manahutu and A. ten Kate, Proceedings of the International Workshop on Membranes in Solvent Filtration, Leuven, Belgium, 2006.
200 http://www.hitk.de/.
201 M. Mutter, Proceedings of the International Workshop on Membranes in Solvent Filtration, Leuven, Belgium, 2006.
202 H. K. Lonsdale, U. Merten and R. L. Riley, *J. Appl. Polym. Sci.*, 1965, **9**, 1341.
203 J. G. Wijmans and R. W. Baker, *J. Membr. Sci.*, 1995, **107**, 1.
204 D. R. Paul, *J. Membr. Sci.*, 2004, **241**, 371.
205 M. Soltanieh and W. Gill, *Chem. Eng. Commun.*, 1981, **12**, 279.
206 H. G. Burghoff, K. L. Lee and W. Pusch, *J. Appl. Polym. Sci.*, 1980, **25**, 323.
207 O. Kedem and A. Katchalsky, *Biochim. Biophys. Acta*, 1958, **27**, 229.
208 K. S. Spiegler and O. Kedem, *Desalination*, 1966, **1**, 311.
209 T. R. Noordman and J. A. Wesselingh, *J. Membr. Sci.*, 2002, **210**, 227.
210 J. P. Robinson, E. S. Tarleton, C. R. Millington and A. Niemeijer, *J. Membr. Sci.*, 2004, **230**, 29.
211 J. Schaep, PhD thesis, University of Leuven, 1999.
212 W. R. Bowen and H. Mukhtar, *J. Membr. Sci.*, 1996, **112**, 263.
213 T. Matsuura and S. Sourirajan, *Ind. Eng. Chem. Proc. Des. Dev.*, 1981, **20**, 273.
214 H. Niemi and S. Paloosaari, *J. Membr. Sci.*, 1994, **91**, 111.
215 B. A. Farnand, F. D. F. Talbot, T. Matsuura and S. Sourirajan, *Ind. Eng. Chem. Proc. Des. Dev.*, 1983, **22**, 179.
216 H. Ohya, H. Jicai and Y. Negishi, *J. Membr. Sci.*, 1993, **85**, 1.
217 D. R. Paul, M. Garcin and W. E. Garmon, *J. Appl. Polym. Sci.*, 1976, **20**, 609.
218 D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, 1970, **14**, 2201.
219 G. H. Koops, S. Yamada and S. Nakao, *J. Membr. Sci.*, 2001, **189**, 241.
220 T. Matsuura, P. Blais, J. M. Dickson and S. Sourirajan, *J. Appl. Polym. Sci.*, 1974, **18**, 3671.
221 T. Matsuura and S. Sourirajan, *J. Appl. Polym. Sci.*, 1972, **16**, 2531.
222 A. Iwama and Y. Kazuse, *J. Membr. Sci.*, 1982, **11**, 297.
223 L. S. White, *J. Membr. Sci.*, 2002, **205**, 191.
224 D. R. Machado, D. Hasson and R. Semiat, *J. Membr. Sci.*, 1999, **163**, 93.
225 D. Bhanushali, S. Kloos, C. Kurth and D. Bhattacharya, *J. Membr. Sci.*, 2001, **189**, 1.
226 M. F. J. Dijkstra, S. Bach and K. Ebert, *J. Membr. Sci.*, 2006, **286**, 60.
227 E. S. Tarleton, J. P. Robinson, C. R. Millington and A. Nijmeijer, *J. Membr. Sci.*, 2004, **230**, 29.
228 T. Tsuru, H. Kondo, T. Yoshioka and M. Asaeda, *AIChE J.*, 2004, **50**, 1080.
229 H. Van Veen and P. Pex, Proceedings of the International Workshop on Membranes in Solvent Filtration, Leuven, Belgium, 2006.
230 G. Bargeman, M. Timmer and C. van der Horst, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, ch. 12, pp. 306–328.
231 S. S. Köseoglu and D. E. Engelgau, *J. Am. Oil Chem. Soc.*, 1990, **67**, 239.
232 L. Lin, K. C. Rhee and S. S. Köseoglu, *J. Membr. Sci.*, 1997, **134**, 101.
233 R. Subramanian, K. S. M. S. Raghavarao, H. Nabetani, M. Nakajima, T. Kimura and T. Maekawa, *J. Membr. Sci.*, 2001, **187**, 57.
234 D. Darnoko and M. Cheryan, *J. Am. Oil Chem. Soc.*, 2006, **83**, 365.
235 *US Pat.*, 4 533 501, 1985.
236 N. Ochoa, C. Pagliero, J. Marchese and M. Mattea, *Sep. Purif. Technol.*, 2001, **22–23**, 417.
237 J. C. Wu and E. Lee, *J. Membr. Sci.*, 1999, **154**, 251.
238 I. Kim, J. Kim, K. Lee and T. Tak, *J. Membr. Sci.*, 2002, **205**, 113.
239 *US Pat.*, 4 787 981, 1988.
240 K. Ebert and F. P. Cuperus, *Membr. Technol.*, 1999, **107**, 5.
241 *Eur. Pat.*, WO9627430, 1996.
242 B. M. Bhosle and R. Subramanian, *J. Food Sci.*, 2005, **69**, 481.
243 B. M. Bhosle, R. Subramanian and K. Ebert, *Eur. J. Lipid Sci. Technol.*, 2005, **107**, 746.
244 H. J. Zwijnenberg, A. M. Krosse, K. Ebert, K. Peinemann and F. P. Cuperus, *J. Am. Oil Chem. Soc.*, 1999, **76**, 83.
245 V. Kale, S. P. R. Katikateni and M. Cheryan, *J. Am. Oil Chem. Soc.*, 1999, **76**, 723.

246 K. K. Reddy, T. Kawakatsu, J. B. Snape and M. Nakajima, *Sep. Sci. Technol.*, 1996, **31**, 1161.
247 E. M. Tsui and M. Cheryan, *J. Food Eng.*, 2007, **83**, 590–595.
248 V. Nwuha, *J. Food Eng.*, 2000, **44**, 233.
249 N. J. Ronde and D. Vogt, in Catalysis by Metal Complexes. Catalyst Separation, Recovery and Recycling, *Chemistry and Process Design*, ed. D. J. Cole-Hamilton and R. P. Tooze, Springer, Dordrecht, The Netherlands, ch. 4, pp. 73–104.
250 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702.
251 J. A. Whu, B. C. Baltzis and K. K. Sirkar, *J. Membr. Sci.*, 1999, **163**, 319.
252 I. F. J. Vankelecom, *Chem. Rev.*, 2002, **102**, 3379.
253 N. Brinkmann, D. Giebel, G. Lohmer, M. T. Reetz and U. Kragl, *J. Catal.*, 1999, **183**, 163.
254 D. de Groot, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Eur. J. Org. Chem.*, 2002, **6**, 1085.
255 A. Datta, K. Ebert and H. Plenio, *Organometallics*, 2003, **22**, 4685.
256 E. L. V. Goetheer, A. W. Verkerk, L. J. P. van den Broeke, E. de Wolf, B. Deelman, G. van Koten and J. T. F. Keurentjes, *J. Catal.*, 2003, **219**, 126.
257 L. J. P. van den Broeke, E. L. V. Goetheer, A. W. Verkerk, E. de Wolf, B. Deelman, G. van Koten and J. T. F. Keurentjes, *Angew. Chem., Int. Ed.*, 2001, **40**, 4473.
258 T. Dwars, J. Haberland, I. Grassert, G. Oehme and U. Kragl, *J. Mol. Catal. A: Chem.*, 2001, **168**, 81.
259 R. Van Heerbeek, P. C. J. Kramer, P. W. N. M. Van Leeuwen and J. N. H. Reek, *Chem. Rev.*, 2002, **102**, 3717.
260 C. Schlenk, A. W. Kleij, H. Frey and G. van Koten, *Angew. Chem., Int. Ed.*, 2000, **39**, 3445.
261 T. J. Dickerson, N. N. Reed and K. D. Janda, *Chem. Rev.*, 2002, **102**, 3325.
262 J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove and G. van Koten, *Nature*, 1994, **372**, 659.
263 C. Müller, M. G. Nijkamp and D. Vogt, *Eur. J. Inorg. Chem.*, 2005, **20**, 4011.
264 G. P. M. van Klink, H. P. Dijkstra and G. van Koten, *C. R. Chim.*, 2003, **6**, 1079.
265 S. Rissom, J. Beliczey, G. Giffels, U. Kragl and C. Wandrey, *Tetrahedron: Asymmetry*, 1999, **10**, 923.
266 G. Giffels, J. Beliczey, M. Felder and U. Kragl, *Tetrahedron: Asymmetry*, 1998, **9**, 691.
267 D. de Groot, E. B. Eggeling, J. C. De Wilde, H. Kooijman, R. J. van Haaren, A. W. van der Made, A. L. Spek, D. Vogt, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1999, **17**, 1623.
268 M. Albrecht, N. J. Hovestad, J. Boersma and G. van Koten, *Chem.–Eur. J.*, 2001, **7**, 1289.
269 E. B. Eggeling, N. J. Hovestad, J. T. B. H. Jastrzebski, D. Vogt and G. van Koten, *J. Org. Chem.*, 2000, **65**, 8857.
270 S. Chavan, W. Maes, L. E. M. Gevers, J. Wahlen, I. F. J. Vankelecom, P. A. Jacobs, W. Dehaen and D. E. De Vos, *Chem.–Eur. J.*, 2005, **11**, 6754.
271 L. W. Gosser, W. H. Knoth and G. W. Parshall, *J. Am. Chem. Soc.*, 1973, **10**, 3436.
272 L. W. Gosser, W. H. Knoth and G. W. Parshall, *J. Mol. Catal.*, 1977, **2**, 253.
273 *US Pat.*, 5 681 473, 1997.
274 K. De Smet, S. Aerts, E. Ceulemans, I. F. J. Vankelecom and P. A. Jacobs, *Chem. Commun.*, 2001, **7**, 597.
275 S. Aerts, H. Weyten, A. Buekenhoudt, L. E. M. Gevers, I. F. J. Vankelecom and P. A. Jacobs, *Chem. Commun.*, 2004, **6**, 710.
276 S. Aerts, A. Buekenhoudt, H. Weyten, L. E. M. Gevers, I. F. J. Vankelecom and P. A. Jacobs, *J. Membr. Sci.*, 2006, **280**, 245.
277 J. Krockel and U. Kragl, *Chem. Eng. Technol.*, 2003, **26**, 1166.
278 P. T. Witte, S. R. Chowdhury, J. E. ten Elshof, D. Sloboda-Rozner, R. Neumann and P. Alsters, *Chem. Commun.*, 2005, **9**, 1206.
279 D. Turlan, E. P. Urriolabeitia, R. Navarro, C. Royo, M. Ménendez and J. Santamaria, *Chem. Commun.*, 2001, **24**, 2608.
280 http://www.membrane-extraction-technology.com/HeavyMetal.php.
281 *US Pat.*, 7 084 284, 2006.
282 D. Astruc, F. Lu and J. R. Aranzes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852.
283 R. Sablong, U. Schlotterbeck, D. Vogt and S. Mecking, *Adv. Synth. Catal.*, 2003, **345**, 333.
284 P. G. N. Mertens, M. Bulut, L. E. M. Gevers, I. F. J. Vankelecom, P. A. Jacobs and D. E. de Vos, *Catal. Lett.*, 2005, **102**, 57.
285 P. G. N. Mertens, I. F. J. Vankelecom, P. A. Jacobs and D. E. De Vos, *Gold Bull.*, 2005, **38**, 157.
286 P. G. N. Mertens, F. Cuypers, P. Vandezande, X. Ye, F. Verpoort, I. F. J. Vankelecom and D. E. De Vos, *Appl. Catal., A*, 2007, **325**, 130.
287 R. M. Gould, L. S. White and C. R. Wildemuth, *Environ. Prog.*, 2001, **20**, 12.
288 L. S. White and A. R. Nitsch, *J. Membr. Sci.*, 2000, **179**, 267.
289 N. A. Bhore, R. M. Gould, S. M. Jacob, P. O. Staffeld, D. McNally, P. H. Smiley and G. R. Wildemuth, *Oil Gas J.*, 1999, **97**, 67.
290 *US Pat.*, 5 651 877, 1997.
291 *US Pat.*, 5 494 566, 1996.
292 *US Pat.*, 5 264 166, 1993.
293 *US Pat.*, 4 678 555, 1987.
294 *Eur. Pat.*, EP 421676, 1991.
295 *US Pat.*, 4 963 303, 1990.
296 *US Pat.*, 4 532 041, 1985.
297 M. Kyburz and W. Meindersma, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, ch. 13, pp. 329–361.
298 Y. Kong, D. Shi, H. Yu, Y. Wang, J. Yang and Y. Zhang, *Desalination*, 2006, **191**, 254.
299 *US Pat.*, 6 488 856, 2002.
300 *US Pat.*, 5 238 567, 1993.
301 *US Pat.*, 4 571 444, 1986.
302 *US Pat.*, 4 532 029, 1985.
303 *US Pat.*, 6 187 987, 2001.
304 *US Pat.*, 5 173 191, 1992.
305 *US Pat.*, 4 810 366, 1989.
306 A. Boam and A. Nozari, *Pharmachem*, 2005(April), 57.
307 *US Pat.*, 7 048 846, 2006.
308 *Eur. Pat.*, WO 02/050212 A3, 2002.
309 X. Cao, X. Y. Wu, T. Wu, K. Jin and B. K. Hur, *Biotechnol. Bioprocess Eng.*, 2001, **6**, 200.
310 D. Shi, Y. Kong, J. Yu, Y. Wang and J. Yang, *Desalination*, 2006, **191**, 309.
311 J. T. Rundel, B. K. Paul and V. T. Remcho, *J. Chromatogr., A*, 2007, doi:10.1016/j.chroma.2007.06.042.
312 J. C. Lin and A. G. Livingston, *Chem. Eng. Sci.*, 2007, **62**, 2728.
313 P. B. Kosaraju and K. K. Sirkar, *J. Membr. Sci.*, 2007, **288**, 41LATER.
314 http://www.kochmembrane.com/selro_pharma.html.
315 *US Pat.*, 5 676 832, 1997.
316 A. G. Fane, in *Nanofiltration. Principles and Applications*, ed. A. I. Schäfer, A. G. Fane and T. D. White, Elsevier, Oxford, 2005, ch. 4, pp. 67–88.
317 I. F. J. Vankelecom, in *Encyclopedia of Chemical Processing*, ed. S. Lee, Marcel Dekker, 2005, 1575–1586.
318 http://www.er.doe.gov/sbir/awards_abstracts/sbir/cycle16/phase2/23.htm.
319 M. Ulbricht, *Polymer*, 2006, **47**, 2217.
320 W. Lequieu and F. E. Du Prez, *Polymer*, 2004, **45**, 749.
321 S. B. Teli, G. S. Gokavi and T. M. Aminabhavi, *Sep. Purif. Technol.*, 2007, **56**, 150.
322 R. Malaisamy and M. L. Bruening, *Langmuir*, 2005, **21**, 10587; C. C. Striemer, T. R. Gaborski, J. L. McGrath and P. M. Fauchet, *Nature*, 2007, **445**, 749.
323 C. C. Striemer, T. R. Gaborski, J. L. McGrath and P. M. Fauchet, *Nature*, 2007, **445**, 749.
324 J. K. Holt, H. G. Park, Y. Wang, M. Stadermann, A. B. Artyukhin, C. P. Grigoropoulos, A. Noy and O. Bakajin, *Science*, 2006, **312**, 1034–1037.