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Department of Chemical Engineering and Chemical Technology

Impacts of spiral-wound membrane modules in organic solvent nanofiltration applications

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By

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Declaration of originality

I, Binchu Shi, hereby certify that the work in this thesis is my own and that the work of others is appropriately acknowledged and referenced.

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Abstract

In recent years organic solvent nanofiltration has showed great potential in a number of industrial fields. A growing number of studies have been reported on development of new membrane materials, optimisation of membrane manufacturing conditions, enhancement of membrane performance and fundamental understanding of molecular transport through membranes. However, studies on spiral-wound membrane modules which are almost exclusively applied in industry are few. In this research project, experimental data on spiral-wound membrane modules of different sizes (from 1.8"x12" to 4.0"x40") in solutions covering a wide range of solute concentrations were collected under steady state operation. Then a procedure to obtain correlations describing fluid dynamics and mass transfer characteristics in the modules was developed using a limited number of experimental data for flat sheets and a 1.8"x12" module only. Furthermore, a multi-scale model for simulating the performance of processes using the modules was developed, considering the molecular transport through the membranes (membrane scale), the fluid dynamics and mass transfer characteristics in the modules (module scale) and the thermodynamic and physical properties of the solutions as a function of operating conditions (process scale). This model was used to simulate the performance of a batch concentration process using different modules under various operating conditions, and good agreement between simulation and experiments was found. In addition, the impact of ultra-high membrane permeance on process efficiency is examined in organic solvent nanofiltration and reverse osmosis as case studies via simulation, considering both concentration polarisation and pressure drops in modules. The key conclusion is that ultra-high permeance membranes will not be able to make a significant impact on process efficiency with current module designs; and the recommendation is that fresh research into module and process design is required.

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Abbreviations

AEPPS	N-aminoethyl piperazine propane sulfonate
ASP	achieved system permeance
BBR	Brilliant Blue R
CA	cellulose acetate
CBMA	carboxybetaine methacrylate
CFD	computational fluid dynamics
DMAEMA	<i>N,N'</i> -dimethylaminoethyl methacrylate
DMF	<i>N,N</i> -dimethylformamide
DMMS	dimethyl methylsuccinate
EA	ethyl acetate
EMET	Evonik Membrane Extraction Technology Limited
GNP	gold nanoparticles
GO	graphene oxide
HFMM	hollow fibre membrane module
IP	interfacial polymerisation
IPA	isopropanol
ISA	integrally skinned asymmetric
IT	irreversible thermodynamics
MEK	methyl ethyl ketone
MOF	metal-organic framework
MW	molecular weight
MWCO	molecular weight cut off

Abbreviations

OSN	organic solvent nanofiltration
PA	polyamide
PAES	poly(arylene ether sulfone)
PAN	polyacrylonitrile
PDMS	poly(dimethylsiloxane)
PE	polyelectrolyte
PEG	polyethylene glycol
PES	polyethersulfone
PF	pore-flow
PI	polyimide
PIB	polyisobutylene
PIM	polymers of intrinsic microporosity
PPSU	polyphenylsulfone
PPy	polypyrrole
PSf	polysulfone
PTMSP	poly[1-(trimethylsilyl)-1-propyne]
PVA	polyvinyl alcohol
R&D	research and development
RO	reverse osmosis
SD	solution-diffusion
SDI	solution-diffusion with imperfections
<i>SEC</i>	specific energy consumption
SoA	sucrose octaacetate
SWMM	spiral-wound membrane module
SY7	Solvent Yellow 7
TFC	thin film composite
TFN	thin film nanocomposite

Abbreviations

THF	tetrahydrofuran
TOABr	tetraoctylammonium bromide
UF	ultrafiltration
UNIF-DMD	Dortmund modified UNIFAC method
VOC	volatile organic chemical
ZIF-8	zeolitic imidazolate framework-8
<i>o</i> -ABA-TEA	<i>o</i> -aminobenzoic acid-triethylamine

Nomenclature

List of symbols

a	coefficient in friction coefficient correlation (dimensionless)
a_i	activity of species i (dimensionless)
A	effective membrane area (m^2)
A_k	the ratio of cross-section pore area to effective membrane area (dimensionless)
b	exponent of Reynolds number in friction coefficient correlation (dimensionless)
C_i	concentration of species i (mol m^{-3})
$\bar{C}_i$	average concentration of the solute i in membrane (mol m^{-3})
D	diffusivity of solute in solvent ($\text{m}^2 \text{s}^{-1}$)
D_i	diffusion coefficient of species i ($\text{m}^2 \text{s}^{-1}$)
D_{ij}^{MS}	multicomponent diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
d_h	hydraulic diameter (m)
d_i	generalised force causing diffusion of species i relative to other species (dimensionless)
F	Faraday constant (coulombs mol^{-1})
F	flowrate ($\text{m}^3 \text{s}^{-1}$)
F_i ($i = 1, 2$)	wall correction factor (dimensionless)
f	friction coefficient (dimensionless)
F_p	permeate flowrate ($\text{m}^3 \text{s}^{-1}$)
F_r	retentate flowrate after modules ($\text{m}^3 \text{s}^{-1}$)
F_r'	retentate flowrate after back pressure valve ($\text{m}^3 \text{s}^{-1}$)
H	height of channel (m)
J	molar flowrate (mol s^{-1})

Nomenclature

J_i	molar permeate flux of species i ($\text{mol m}^{-2} \text{s}^{-1}$)
J_{tot}	total volumetric permeate flux ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)
$\tilde{J}$	local permeate molar flowrate through element (mol s^{-1})
k	mass transfer coefficient (m s^{-1})
k_D	permeability coefficient in Darcy's law ($\text{m}^2 \text{s}^{-1} \text{Pa}^{-1}$)
K_{HP}	coefficient in Hagen–Poiseuille model (dimensionless)
K_i	sorption coefficient (dimensionless)
l	thickness of the membrane selective layer (m)
L	length of channel (m)
L_i	coefficient of proportionality ($\text{mol}^2 \text{m}^{-1} \text{s}^{-1} \text{J}^{-1}$) or mechanical permeability coefficient for imperfections in membranes ($\text{m s}^{-1} \text{Pa}^{-1}$)
$L_{j,simple}$	permeability coefficient of solvent j in simplified solution-diffusion model ($\text{m s}^{-1} \text{Pa}^{-1}$)
L_p	mechanical filtration coefficient of the membrane ($\text{m s}^{-1} \text{Pa}^{-1}$)
$\overline{L_p}$	specific hydraulic permeability ($\text{m}^2 \text{s}^{-1} \text{Pa}^{-1}$)
L_P	permeate channel length (m)
$L_{s,t}$	solute loss to permeate at time t (dimensionless)
W_P	permeate channel width (m)
L_V	mechanical permeability coefficient for perfect membrane matrix ($\text{m s}^{-1} \text{Pa}^{-1}$)
M_i	molecular weight of species i (g mol^{-1})
n_i	mass flux of species i ($\text{kg m}^{-2} \text{s}^{-1}$)
N_L	number of membrane leaves (dimensionless)
P	pressure (Pa)
P_i	permeability coefficient of species i ($\text{mol m}^{-2} \text{s}^{-1}$)
$P_{i,imp}$	diffusional permeability coefficient of imperfections ($\text{m}^2 \text{s}^{-1}$)
$\overline{P}_l$	local solute permeability coefficient (m s^{-1})
P_m	membrane permeance ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)
Q	quantity of experimental data (dimensionless)

Nomenclature

r_p	pore radius (m)
r_s	sphere radius (m)
R	ideal gas constant ($\text{Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$)
Re	Reynolds number (dimensionless)
Rej_i	observed rejection of species i (%)
S_C	steric hindrance factor for convection (dimensionless)
S_D	steric hindrance factor for diffusion (dimensionless)
S_p	standard deviation of pore size distribution (dimensionless)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
$resnorm$	the norm of residuals (dimensionless)
T	temperature (K)
t	permeation time (s)
u	linear velocity of flow (m s^{-1})
$\bar{u}$	average linear velocity of flow (m s^{-1})
V	permeate volumetric flowrate ($\text{m}^3 \text{s}^{-1}$) or volume (m^3)
w_i	mass fraction of species i (dimensionless)
W	width of the channel (m)
x	direction from feed side to permeate side through membrane (dimensionless)
x_i	molar fraction of species i in solution (dimensionless)
$\tilde{x}$	local solute molar fraction in solution through element (dimensionless)
$\bar{x}$	average solute molar fraction (dimensionless)
z_i	valence of species i (dimensionless)
$z_{q,c}$	calculated data
$\overline{z_{q,e}}$	average experimental data
ΔC_i	concentration difference across membrane (mol m^{-3})
ΔP	pressure drop or pressure difference across membrane (Pa)

Nomenclature

ΔP_{TM}	transfer membrane pressure (Pa)
Δx^i	length of element $i \times j$ along x axis (m)
ΔX	pore length (m)
Δy^j	length of element $i \times j$ along y axis (m)

Greek symbols

α	coefficient in Sherwood number correlation (dimensionless)
β	exponent of Reynolds number in Sherwood number correlation (dimensionless)
λ	exponent of Schmidt number in Sherwood number correlation (dimensionless)
ρ	mass density (kg m^{-3})
ρ_M	molar density of solvent-solute-membrane mixture (mol m^{-3})
η	dynamic viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
μ_i	chemical potential of species i (J mol^{-1})
v_i	molar volume of species i ($\text{m}^3 \text{mol}^{-1}$)
ε	membrane porosity or void fraction in spacer-filled channel (dimensionless)
τ	membrane tortuosity (m)
γ_i	activity coefficient of species i (dimensionless)
σ_i	reflection coefficient (dimensionless)
χ_{im}	friction coefficient between solute and membrane (dimensionless)
χ_{iv}	friction coefficient between solute and solvent (dimensionless)
$\Delta\pi$	osmotic pressure difference across membrane (Pa)

Subscripts

f	feed solution or feed channel
fm	feed side membrane-liquid interface

Nomenclature

F	local feed channel in element
i	solute
j	solvent
p	permeate solution or permeate channel
P	local permeate channel in element
r	retentate
R	local retentate channel in element
s	solute
V	solvent
(m)	membrane phase

Superscripts

i	position i in the direction of x axis
j	position j in the direction of y axis
MS	Maxwell-Stefan

Chapter 1

Introduction

Organic solvent nanofiltration (OSN) is an emerging technology which applies solvent resistant membranes in organic solutions to separate molecules between 200 and 2,000 g mol⁻¹. It distinguishes itself from other conventional separation technologies such as distillation and extraction by its high energy efficiency, milder operating conditions, less waste and higher sustainability. In recent years a rapidly growing number of studies have been reported on the development of new membrane materials, optimisation of membrane manufacturing conditions, enhancement of membrane performance and fundamental understanding of molecular transport through membranes. These studies have shown the great potential of this novel technology in the chemical and pharmaceutical industry, for a variety of applications such as recovery and purification of pharmaceuticals [1, 2], solvent exchange [3], separation of base chemicals [4, 5], purification and concentration of consumer chemicals [6, 7], concentration and purification of specialty chemicals [8], and catalyst recycle [9]. However, most of these studies focused on flat sheet membranes; studies on membrane modules which are used for applications in industry are few.

In industry, the smallest membrane unit in which membranes are packed is usually called a membrane module. The design of a membrane module is critical for the performance of membrane processes. The main design criteria are: (1) high membrane packing density (the ratio of membrane area to module volume), to minimise capital costs and plant size; (2) efficient mass transfer, to minimise concentration polarisation and fouling; (3) minimum pressure drop through membrane modules, to minimise the loss of driving force; (4) good contact between fluids and membranes, to minimise dead areas; and (5) easy

manufacturing, operation and cleaning. Today, there are five main membrane module designs available in the market: plate-and-frame, spiral-wound, tubular, capillary and hollow fibre. Plate-and-frame modules are the earliest version of membrane modules. In this module, sets of membrane plates where two membranes are placed in a sandwich-like fashion with their permeate sides facing each other are located in a frame. Spacers are used between membranes to create flow paths. This module design offers the ability to exchange a single membrane and has low sensitivity to particulate blocking of feed channels. However, it has low packing density. Spiral-wound membrane modules (SWMMs) are another membrane module design where flat sheet membranes and spacers are wrapped around a central perforated tube. The packing density in this module design is significantly improved. The latter three module designs are the assembly of tubular, capillary or hollow fibre membranes, respectively. Distinctly from flat sheet membranes, these cylindrical membranes are packed in large bundles in a pressure vessel. Hollow fibre membrane modules (HFMMs) have the highest packing density due to the small diameter of hollow fibre membranes, however they usually suffer from low mass transfer, high pressure drop and low pressure tolerance. Among these five main module designs, SWMMs stand out due to their good balance between high packing density, ease of operation, low pressure loss, good contact between fluids and membranes, and less tendency for fouling [10, 11]. In practice, SWMMs are almost exclusively used in large-scale OSN applications.

The impacts of SWMMs on the performance of OSN processes are critical, but have not been thoroughly investigated. Firstly, experimental data for SWMMs in OSN applications are few, although considerable and successful laboratory studies on flat sheet membranes have been reported. Perfect performance of flat sheet membranes does not necessarily mean good performance of SWMMs. This is due to the difference in configuration between flat sheet membranes and SWMMs, causing different extents of concentration polarisation and pressure drop. Therefore, the lack of SWMM data can to some extent weaken the confidence of the industries on this novel technology. Secondly, the fluid dynamics and mass transfer characteristics are critical for membrane performance due to the occurrence of concentration polarisation

and pressure drop, however these characteristics in SWMMs for OSN applications have not been deeply understood. Distinctly from aqueous applications, the variety of the components of interest in OSN applications results in a wide range of thermodynamic and physical properties of the solutions, thus making the characterisation of the fluid dynamics and mass transfer even more complicated. Thirdly, there is a lack of reliable process models which can consider the molecular transport through membranes, the fluid dynamics and mass transfer characteristics in SWMMs, and the thermodynamic and physical properties of the solution of interest as a function of operating conditions. Without a reliable process model, the scale-up and optimisation of OSN processes is usually more time-consuming, expensive and difficult. In this research project, the challenges mentioned above have been addressed. The results from this research can strengthen the confidence of industries in OSN technology and to some extent counteract the general hesitancy of the industries to change established processes. The main structure of this research is outlined below.

Chapter 2 presents a fundamental introduction to OSN technology including OSN membranes, SWMMs and performance characterisation methods. The main OSN applications using SWMMs are reviewed and their advantages compared to conventional technologies are commented upon. The studies on the transport mechanisms in OSN applications are also discussed, at three different scales:

- (1) membrane scale. The fundamental mechanisms of molecular transport through membranes are explained and their mathematical models are presented. The feasibility of these mechanisms and mathematical models for OSN applications is also commented upon;
- (2) module scale. The studies on the fluid dynamics and mass transfer characteristics in SWMMs are reviewed, and the limitations of these studies in OSN applications are pointed out;
- (3) process scale. The process models proposed for specific OSN applications are reviewed, and the limitations of these models to account for the impact of SWMMs on process performance are commented upon.

In Chapter 3, experimental performance for SWMMs of different sizes ranging from 1.8"x12" to 4.0"x40" in processing solutions of sucrose octaacetate in ethyl acetate (SoA / EA) with a wide range of SoA concentration (0 – 20 wt%) under various operating conditions is investigated. Furthermore, a procedure is developed to describe the fluid dynamics and mass transfer characteristics in a specific SWMM by regression of a limited number of experimental data for flat sheets and a 1.8"x12" SWMM only. With this procedure, it is not necessary to know a priori the spacer geometry which is usually confidential for end users, because the necessary information about the spacer geometry will be also obtained from the regression. This procedure is applied here to obtain the correlations for describing the fluid dynamics and mass transfer characteristics in a 1.8"x12" PuraMem® S600 SWMM, and the obtained correlations are used to predict the performance of other SWMMs made using the same spacers but larger sizes (2.5"x40" and 4.0"x40") and / or different types of membranes in the same solutions (SoA / EA solutions) under various operating conditions. Good agreement between simulation and experiments demonstrates the feasibility of this procedure.

In Chapter 4, a process model is developed using the "OSN Designer" software tool. This software tool makes OSN unit operations available in process modelling environments such as Aspen Plus, HYSYS and ProSim Plus. The proposed process model accounts for the molecular transport through membranes (membrane scale), the fluid dynamics and mass transfer characteristics in SWMMs (module scale), and thermodynamic and physical properties of solution of interest, as a function of operating conditions (process scale). Furthermore, this process model is used to predict the performance of an OSN batch process to concentrate SoA / EA solutions using three SWMMs with different sizes under various operating conditions. Since the SWMMs and the solutions used here are the same ones used in Chapter 3, the correlations for describing the fluid dynamics and mass transfer characteristics in the SWMMs, are taken from Chapter 3. Good agreement between the experiments and the simulation not only verifies the feasibility of the process model but also shows the potential to predict the performance of any OSN process which uses SWMMs, based on simple flat sheet test data. In addition, the effects of concentration

polarisation, pressure drops through feed and permeate channels and thermodynamic non-ideality of the solution on large scale batch concentration are also investigated.

In Chapter 5, the potential impact of ultra-high permeance membranes on the efficiency of industrial processes is examined via simulation, based on the knowledge obtained from previous chapters. Initially, the performance of flat sheet membranes in cross-flow cells is simulated in order to understand the effect of concentration polarisation in the absence of pressure drop. Afterwards, the performance of SWMMs in pure solvent in the absence of concentration polarisation is simulated, in order to investigate the effect of the pressure drop in the module on the overall module performance. Then, the performance of modules made of membranes with various permeance in the solutions is evaluated. In this case, it is shown how the module performance is strongly limited by the combined effects of concentration polarisation and pressure drop. Finally, the simulation is performed at the process scale using SWMMs, in order to investigate whether high permeance membranes can lead to more efficient (i.e. faster or more productive) processes. The attempts that have been reported in the literature to overcome the limitations of concentration polarisation and pressure drop are also summarised and explained in terms of technological characteristics and energy requirements. In addition, the advantages and limitations of other main membrane module designs are discussed, with special emphasis on the popular hollow fibre configuration, which offers the highest packing density among membrane modules.

In Chapter 6, the main results from this research are summarised and future perspectives in this field are outlined.

Chapter 2

Literature review

2.1 Organic solvent nanofiltration membranes and membrane modules

Separation processes account for 40 – 70 % of both capital and operating costs in chemical industries and the main separation technologies in industry are adsorption, extraction, crystallization, distillation, evaporation, chromatography and membrane technologies [12]. Membrane technology as a relatively young technology compared to the others, which has been gradually used for industrial applications since the late 1960s, and distinguished itself in terms of economy, environment and safety. Initially, membranes were largely limited to aqueous applications such as water softening and micropollutant removal and could not be applied in organic solvents due to lack of chemical stability. Recently, a new paradigm technology, organic solvent nanofiltration (OSN), also known as solvent resistant nanofiltration, emerged to address efficient separations in organic solvents. OSN is a pressure driven process using membranes made of solvent stable materials and allows molecular separation in the range of 200 – 2,000 g mol⁻¹ in non-aqueous environments.

OSN membranes can be classified into two main families: ceramic and polymeric membranes. The former is usually made of metal oxides such as alumina, zirconia, titania or mixed oxides and possesses an asymmetric structure composed of two or more porous layers. Generally speaking, the ceramic membranes have less swelling in most of the solvents and less compression under pressure, compared to the polymeric membranes, due to the nature of ceramic materials, however they usually have lower permeance and looser structure [13]. In addition, they are relatively more expensive to scale up. On the other hand,

polymeric membranes benefited from their large variety of available materials and ease of fabrication and scale-up and so have been used in various OSN applications: the recovery and purification of pharmaceuticals [1, 2], solvent exchange [3], separation of base chemicals [4, 5], purification and concentration of consumer chemicals [6, 7], concentration and purification of specialty chemicals [8], and catalyst recycle [9]. Their great potential in concentration and purification processes has been recognised [13 – 15].

Polymeric membranes can be subdivided into two main groups: integrally skinned asymmetric (ISA) membranes and thin film composite (TFC) membranes. The former is formed by the phase inversion technique where a casting solution is precipitated on a non-woven backing made of solvent-stable polymers such as polypropylene, polyester and polyacrylonitrile [16]. The precipitated layer possesses a skin layer on top of a more porous sublayer made of the same materials. The latter one is composed of a thin selective layer on the top of a support which is usually an ultrafiltration (UF) polymeric membrane made of different materials by phase inversion. The common methods to form the thin selective layer are interfacial polymerisation [17] and coating [18] at the surface of the support. The TFC membranes are usually characterised by some freedom in their design for a specific application and the relatively higher permeance with similar tightness compared to ISA membranes, deriving from the thinner selective layer. Their performance can be further improved by adding nanomaterials [19 – 21]. At present, many polymeric OSN membranes including both ISA membranes such as SolSep® series from SolSep BV, PuraMem® series and DuraMem® series from Evonik Membrane Extraction Technology Limited (EMET), and TFC membranes such as PuraMem® S600 from EMET and GMT membranes from GMT Membrantechnik GmbH, are available in the market [13].

Membrane modules are used in industry to package higher areas of membranes. There are five main membrane module designs: plate-and-frame, spiral-wound, tubular, capillary and hollow fibre modules. The first two are flat sheet membrane assembly while the others originated from cylindrical (“tube”)

membranes. Among these module designs, spiral-wound membrane modules (SWMMs) are the most popular in aqueous applications ranging from reverse osmosis (RO) to UF, such as desalination, water reclamation, treatment of industrial wastewater and product treatment in dairy industry, due to their good balance between high membrane packing density, ease of operation, low fouling tendency and low cost [15]. In fact, SWMMs are almost exclusively used in OSN as well.

As shown in Figure 2.1, a SWMM consists of membrane leaves wound around a central perforated tube (through which the permeate exits the module); feed and permeate spacers are used to support the membrane and generate the channels for feed and permeate flows, respectively, while an anti-telescoping device and an outer wrap are used to secure the assembly [13, 22]. The feed fluid is forced to flow longitudinally through the feed channel, usually across feed spacers that both hold the membrane leaves apart and promote turbulence and mass transfer; while the permeate flows inwards to the central collection tube through the permeate spacer, which resists the applied pressure forcing the membranes together.

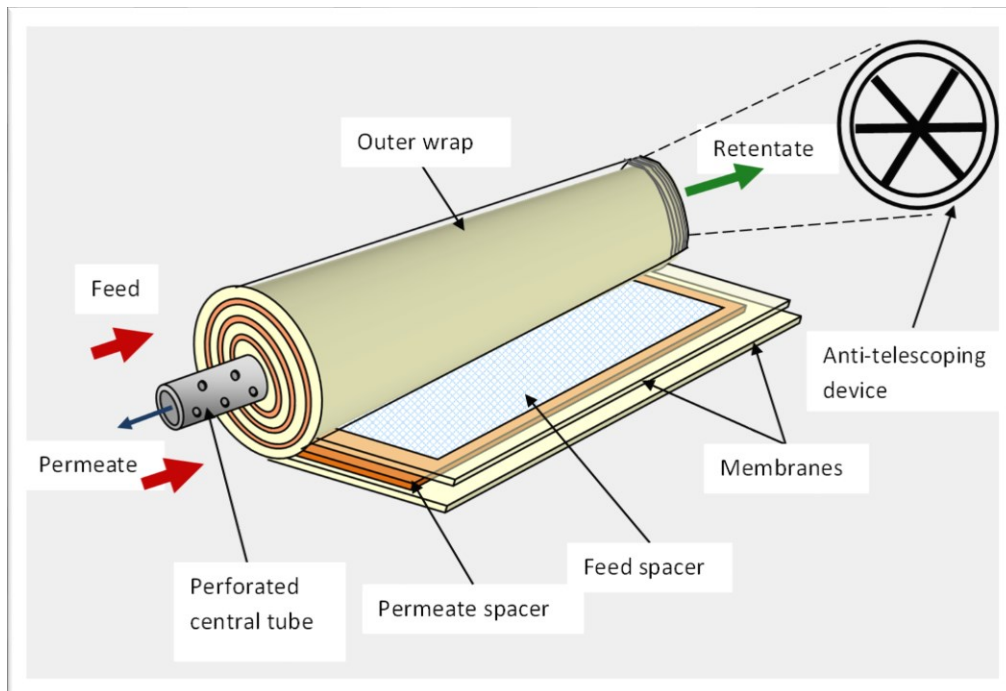


Figure 2.1: Schematic diagram of a spiral-wound membrane module (adapted from [13, 22]).

The performance of both membranes and modules is characterised by two key parameters: rejection and permeate flux. The rejection of a species i (Rej_i) is calculated using Equation (2.1):

$$Rej_i = \left(1 - \frac{C_{ip}}{C_{ir}}\right) \cdot 100\% \quad \text{Equation (2.1)}$$

C_{ir} and C_{ip} are the concentrations of the species i at retentate side and permeate side, respectively. The permeate flux (J_{tol}) is calculated using Equation (2.2):

$$J_{tol} = \frac{V}{t \cdot A} \quad \text{Equation (2.2)}$$

V is the total permeate volume collected during the permeation time t , and A is the effective membrane area. To account for the effect of pressure on the permeate flux, the permeance (P_m) defined as the ratio of permeate flux to transmembrane pressure (ΔP_{TM}) is also used (see Equation (2.3)).

$$P_m = \frac{J_{tol}}{\Delta P_{TM}} \quad \text{Equation (2.3)}$$

2.2 Applications of spiral-wound membrane modules in OSN

Primarily, research activities in the field of OSN have been focused on the development of new materials stable in organic solvents and harsh conditions, while the studies on scaled-up industrial applications are still few. This section overviews the main applications of SWMMs in OSN, from pilot plant to industrial scales, and compares OSN with other conventional technologies.

2.2.1 Max-Dewax process

Lubricant production is one of the most energy intensive processes in the refining industry, and solvent lube oil dewaxing processes are practiced world-wide. As shown in Figure 2.2(a) [23], in the conventional

dewaxing process, waxy feed (the mixture of wax and lube oil) is first dissolved in a light hydrocarbon solvent mixture for example, a blend of methyl ethyl ketone (MEK) and toluene, then the mixture of the feed and the solvent is refrigerated to a desired temperature ($-18 - 0\text{ }^{\circ}\text{C}$) by successive cooling and refrigeration until the wax crystals precipitate. Then the chilled feed mixture is separated into two main intermediate products (a lube oil filtrate and a slack wax mix) by using a set of rotating drums. The lube oil filtrate containing the lube oil and most of the solvent is distilled to get high quality lube oil. The solvent vapour is then condensed and refrigerated to the low temperature and re-used to dissolve the waxy feed. The solvent in the slack wax mix is recovered in a similar manner. In addition, substantial solvent is required in the solvent lube oil process, typically four to five cubic meters of solvent is recirculated to produce one cubic meter of lube oil. Therefore, a large amount of energy is consumed for the solvent recovery.

Significant equipment and energy savings can be realised by recovering cold solvent directly from the lube oil filtrate using membranes (see Figure 2.2(b) [23]). White and Nitsch [24] manufactured a polyimide membrane using a co-polymer of diaminophenylindane with benzophenone tetracarboxylic dianhydride at laboratory scale and the membrane demonstrated recovery of the chilled solvent from the lube filtrates at a purity of better than 99% with a good and steady flux over two months. This success led to installation of a demonstration plant at Mobil's Beaumont refinery in 1994 [25]. In this demonstration plant six module arrays, each containing six spiral-wound membrane modules made of the polyimide membranes and connected in series, were installed. It was designed to treat 600 m^3 of the lube oil filtrate per day. ExxonMobil Corporation and W.R. Grace initiated a steady-state run in May 1995 and shut down the system in August 1996 after successfully meeting all programme objectives. During the period, the permeate flux slowly decreased from about $7\text{ m}^3\text{ h}^{-1}$ to $4\text{ m}^3\text{ h}^{-1}$ while the oil rejection was kept at about 99% except during the short initial start-up. The successful completion of the demonstration stage led to a commercial process, trademarked as Max-Dewax at the Beaumont refinery in 1998 [23 – 25]. The Max-Dewax process typically takes $5,800\text{ m}^3\text{ day}^{-1}$ of lube oil filtrate and returns $1 - 1.5\text{ m}^3\text{ day}^{-1}$ of purified chilled solvent to the wax crystallization process. Although the Max-Dewax has been shut down after

Hurricane Katrina, it was operated for several years and remains as the largest membrane separator of organic liquids in the world.

In comparison to the conventional process, the Max-Dewax process increased average base oil production by over 25 % and improved dewaxed oil yields by 3 – 5 %. In addition, significant energy consumption (20 % per unit volume of product) was saved. All these contributed to a net uplift profitability of 6.1 million US dollars per year which paid back the capital expenditure in less than one year. From the environmental point of view, a large amount of cooling water was saved because the solvent did not need to be cooled prior to re-use, and the thermal pollution associated with such cooling water use was reduced. Besides, the loss of dewaxing solvents, which are volatile organic chemicals (VOCs), into the environment was also decreased.

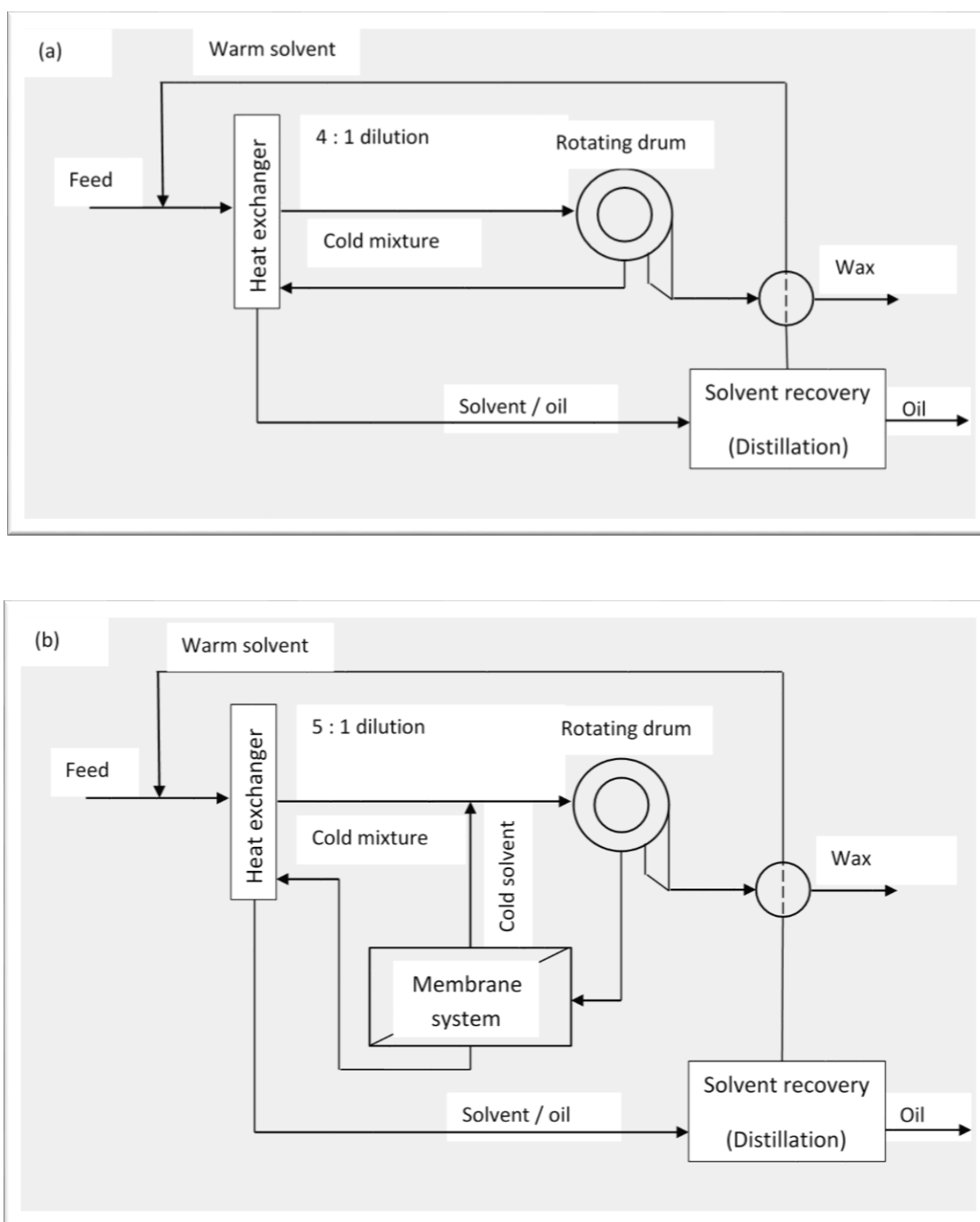


Figure 2.2: Schematic diagrams of a solvent lube oil dewaxing process: (a) a conventional process; (b) a membrane-enhanced process (Adapt from Gould et al. [23]).

2.2.2 Purification of active pharmaceutical ingredients at Janssen Pharmaceutica N.V.

Impurities are a hurdle in many pharmaceutical and nutraceutical production processes, where tiny amounts of impurities can adversely affect end-product quality. At Janssen Pharmaceutica N.V., during the synthesis of a macrocyclic intermediate of a new drug (API-INT, molecular weight (MW) = 675 g mol⁻¹), its

isomer (Isomer B) and a series of oligomeric impurities based on API-INT with $MW > 1,000 \text{ g mol}^{-1}$ (i.e., dimers, trimers, tetramers, pentamers, etc.) are also formed. Conventional technologies such as distillation and evaporation are not capable of purifying the product since API-INT has similar physical properties as the impurities and is also sensitive to temperature. Preparative high pressure chromatography can separate Isomer B and dimers and trimers of API-INT, however it is tedious for oligomeric impurities such as tetramers and higher oligomers of API-INT, since these high oligomers block the active sites of the stationary phase. Compared to these conventional techniques, membrane separations give the possibility for achieving the purification goal since they separate the components based on molecular size under relatively milder conditions.

Sereewatthanawut et al. [26] applied a 1.8"x12" SWMM made of DuraMem® 1000 membranes to purify a feed solution containing 26 g L^{-1} of API-INT, 7.2 g L^{-1} of Isomer B and 1.9 g L^{-1} of oligomeric impurities in tetrahydrofuran (THF) in a constant volume diafiltration mode. The module showed >99 % rejection of tetramer and pentamer impurities, about 93 – 96 % rejection of dimer and trimer and about 60 % rejection of API-INT. The filtrate containing 8.4 g L^{-1} of API-INT, 2.1 g L^{-1} of Isomer B and $\leq 0.2 \text{ g L}^{-1}$ of oligomeric impurities was then sent to a solvent recovery stage where two 1.8"x12" SWMMs made of DuraMem® 300 membranes were applied to further purify API-INT and to recover the solvent, which was sent back to the diafiltration process. This dual system (see Figure 2.3) provided a product with 2.4 % of oligomeric impurities (better than the goal of 3 %) and recovered $\geq 98 \%$ of API-INT. In addition, a large amount of the solvent was saved from the solvent recovery stage which further benefited the process.

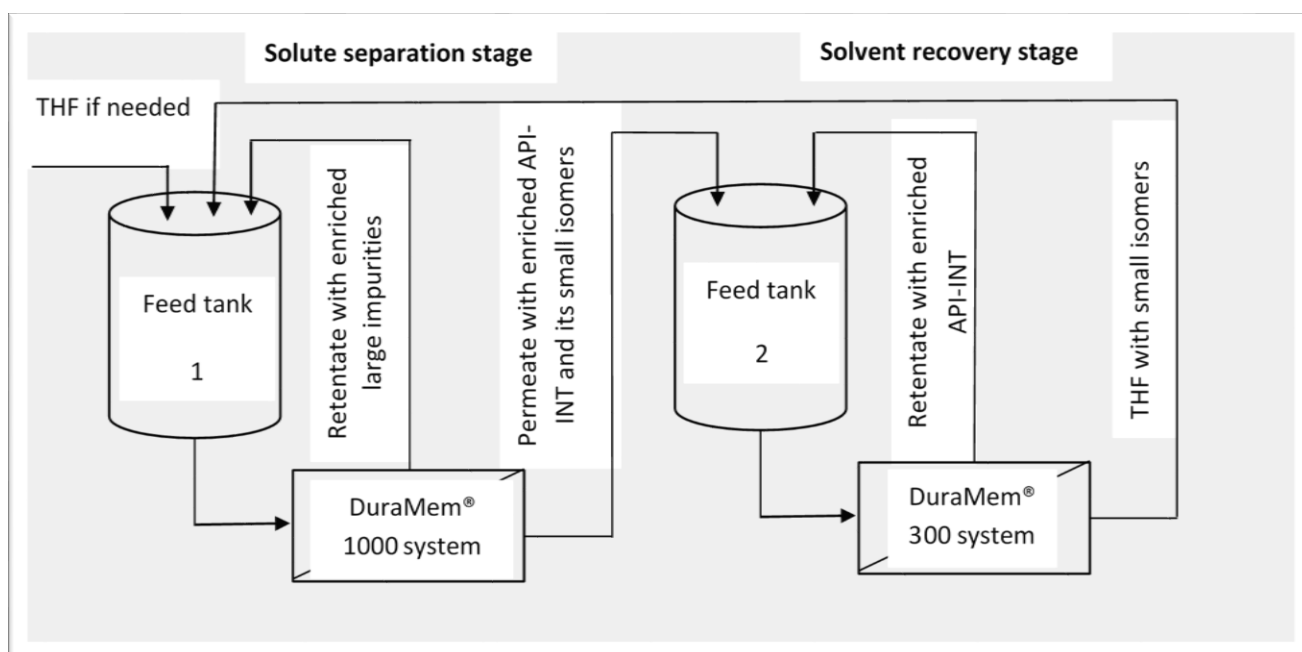


Figure 2.3: Schematic diagram of a dual membrane system for separating API-INT from its small isomers and large impurities in THF at Janssen Pharmaceutica N.V. (Adapt from Sereewatthanawut et al. [26]).

2.2.3 Other OSN applications in mock solutions

In pharmaceutical and high value natural compound production, a product solution typically contains a product and relatively higher MW impurities. To unveil the potential of OSN in these productions, Sereewatthanawut et al. [26] mimicked a typical solution using 4-phenylazophenol, Solvent Yellow 7 (SY7, MW = 198.2 g mol⁻¹) and Brilliant Blue R (BBR, MW = 826.0 g mol⁻¹) as model product and impurity compounds, respectively, and a typical industrial solvent, N,N-dimethylformamide (DMF). The aim was to purify the solution consisting of 10 g L⁻¹ of SY7 and 1 g L⁻¹ of BBR, and to provide a final product with ≥ 99.5 % of SY7 with at least 90 % recovery. They applied a constant volume diafiltration using a 1.8"x12" spiral-wound DuraMem® 300 membrane module to realise the task, and fresh DMF was used as a diafiltration solvent. After ten diafiltration volumes, a high product purity of 99.7 % and a product yield of 90 % were achieved.

Some studies [27, 28] also reported the performance of SWMMs in organic solutions in steady state operation where permeate was recirculated back to the feed tank. These studies covered a wide range of

solvents and operating conditions and illustrated the possibility of applying OSN in industry. Silva et al. [27] reported the performance of a 2.5"x40" spiral-wound StarMem® 122 membrane module in solutions of tetraoctylammonium bromide (TOABr) in toluene. The feed pressure, retentate flowrate and feed concentration were monitored to investigate the performance of the module, and a permeance of 1 – 2 L m⁻² h⁻¹ bar⁻¹ and almost complete rejection of TOABr were reported. Sairam et al. [28] tested a 1.8"x12" SWMM made of laboratory-fabricated polyaniline membranes in acetone, THF and DMF. This module gave a stable permeance with molecular weight cut off (MWCO) of 150 – 300 g mol⁻¹, which was characterised by oligostyrene standards.

2.3 Development of process models for OSN applications

The development of membrane processes usually involves several stages, starting from feasibility tests at laboratory scale, passing through pilot plant tests, and finishing with industrial scale processes. A fundamental understanding of the basic separation mechanism and a reliable modelling framework are crucial to meet the growing needs and applications, and enable the scale-up to be efficient and economic [29]. An adequate model for OSN processes can be divided into three scales: molecular transport mechanisms through membranes, fluid dynamics and mass transfer in modules and process simulation [30]. Accordingly in the development of the model, the following problems have to be resolved: (i) selection of a membrane transport mechanism adequate to describe the molecular transport across the membrane; (ii) knowledge of the fluid dynamics and mass transfer characteristics in the module; (iii) availability of the thermodynamic and physical properties of the solutions as a function of operating conditions. Studies which have focused on addressing these three problems are reviewed in Sections 2.3.1, 2.3.2 and 2.3.3, respectively.

2.3.1 Membrane transport mechanisms and their applications in OSN

During the past few decades, substantial effort and time has been devoted to understanding the transport mechanisms through OSN membranes [31 – 87]. These transport mechanisms can be classified into four

main families: irreversible thermodynamics (IT), solution-diffusion (SD), pore-flow (PF) and solution-diffusion with imperfections (SDI) mechanisms. Table 2.1 gives an overview of the applications of these mechanisms in the systems using various membranes, solvents and solutes. The details of these mechanisms, mathematical models and applications in OSN are reviewed below.

Table 2.1: Applications of different membrane transport mechanisms and mathematical models in OSN

Transport mechanisms	Mathematical models	Membranes and chemicals			Reference
		Materials of membrane	Solvents	Solutes	
		selective layer			
IT	Spiegler-	PDMS	Xylene	Low-polarity organic compounds	[34]
	Kedem	CA	Ethanol, hexane	Linear hydrocarbons, linear carboxylic acids	[35]
		PA, poly(piperazine-amide)	Ethanol-water mixture	Glucose, proline, tyramine, tartaric acid, NaCl	[36]
SD	Classical SD	PI	Toluene	n-Decane, n-hexadecane, n-docosane, pristane, 1-methyl-naphthalene, 1-phenylundecane	[37]
		PI	Methanol, toluene, EA	-	[38]
		PI	Toluene	TOABr, docosane	[39]
	Simplified SD	PI, PDMS	Methanol	DMMS	[40]
		PDMS, PDMS-silicone	Toluene, phenol, water	-	[41]
		PDMS	Hexane	Sunflower oil, PIB	[42]
		PDMS	Ethanol, toluene, n-heptane	-	[43]
	Maxwell-	Silicone	Alcohols	Dyes (300 – 1000 g mol ⁻¹)	[44]
	Stephan	PI	EA, isopropanol, toluene, ethanol	-	[45]

Chapter 2 Literature review

PF	Log-normal	Poly(piperazine-amide), PA, sulphonated PES	Water	Uncharged organic compounds	[46]
		PDMS, PA, TiO ₂	Methanol, ethanol, acetone, EA, n-hexane	Eusolex, 2,2-methylene-(6-tert-butyl-4-methylphenol), Victoria Blue, DL- α -tocopherol hydrogen succinate, bromothymol blue, erythrosine B	[47]
	SHP	PI, PDMS, PA	Methanol	Quaternary alkyl ammonium bromide salts	[48]
	Ferry	PI, PDMS, PA	Methanol	Quaternary alkyl ammonium bromide salts	[48]
	Verniory	PI, PDMS, PA	Methanol	Quaternary alkyl ammonium bromide salts	[48]
	SF-PF	PDMS, polyamide	Alcohols, alkanes	Organic dyes, triglycerides	[49]
	HP	PDMS	Aromatic solvents, alcohols, alkanes	-	[50]
		PDMS	Alcohols, alkanes	-	[51]
SDI	SDI	PDMS	Pentane-decane, pentane-dodecane	-	[52]

2.3.1.1 Irreversible thermodynamics (IT) mechanisms and their applications in OSN

The irreversible thermodynamics (IT) mechanism considers transport as an irreversible process during which free energy is dissipated continuously and entropy is produced. The first two IT models are the Kedem-Katchalsky [53] and Spiegler-Kedem [54] models, which were used to describe ion transport through nanofiltration membranes [55]. According to the Kedem-Katchalsky model, the solvent and solute fluxes (J_{tol} and J_i , respectively) are described by the following equations:

$$J_{tol} = L_p(\Delta P - \sigma_i \Delta \pi) \quad \text{Equation (2.4)}$$

$$J_i = P_i \Delta C_i + (1 - \sigma_i) J_{tol} \bar{C}_i \quad \text{Equation (2.5)}$$

L_p is the mechanical filtration coefficient of the membrane (also known as local permeability coefficient, or hydraulic permeability), and P_i is the permeability coefficient of the solute i . σ_i is the reflection coefficient, corresponding to the solute fraction rejected by the membrane. $\sigma_i = 1$ means complete rejection of the solute i while $\sigma_i = 0$ is no rejection of the solute i at all. ΔP and ΔC_i are the difference of the pressure and the concentration of the solute i across the membrane, respectively. $\bar{C}_i$ is the average concentration of the solute i in the membrane and $\Delta \pi$ is the osmotic pressure difference across the membrane. When the solvent flux is too high and / or the concentration gradient through the membrane is too big, the difference of the concentration, osmotic pressure and hydraulic pressure through the membrane shown in Equations (2.4) and (2.5) is not adequate to describe the solvent and solute transport. For this reason, Spiegler and Kedem [54] introduced the differentiating definitions, specific hydraulic permeability (also known as intrinsic membrane permeability, $\bar{L}_p$) and local solute permeability coefficient ($\bar{P}_i$), to the Kedem-Katchalsky model for these cases. Their mathematical model is known as Spiegler-Kedem model and can be described as Equations (2.6) and (2.7).

$$J_{tol} = \bar{L}_p \left(\frac{dP}{dx} - \sigma_i \frac{d\pi}{dx} \right) \quad \text{Equation (2.6)}$$

$$J_i = -\bar{P}_i \frac{dC_i}{dx} + (1 - \sigma_i) J_{tol} \bar{C}_i \quad \text{Equation (2.7)}$$

x refers to the direction from feed side to permeate side through a membrane. C_i is the concentration of species i . The first and second terms in Equation (2.7) represent the contributions of diffusion and convection, respectively. The local solute permeability and reflection coefficient can be obtained by fitting of experimental rejection versus flux, according to Equations (2.8) and (2.9).

$$Rej_i = \frac{(1 - F) \cdot \sigma_i}{1 - \sigma_i F} \quad \text{Equation (2.8)}$$

$$F = e^{\frac{-J_{tol}(1-\sigma_i)}{\bar{P}_i}} \quad \text{Equation (2.9)}$$

The Spiegler-Kedem model was successfully applied to describe the transport of organic components in several studies: Robinson et al. [34] used the model to explain the transport of low-polarity organic solvent (xylene) and solutes (MW = 84 – 611 g mol⁻¹) through poly(dimethylsiloxane) (PDMS) membranes; Koops et al. [35] described the transport of linear hydrocarbons and linear carboxylic acids in ethanol and hexane through cellulose acetate (CA) membranes; Labanda et al. [36] satisfactorily described the permeation of four organic solutes (glucose, proline, tyramine and tartaric acid) in aqueous and ethanol solutions through both polyamide (PA) and poly(piperazine-amide) based membranes. However, this model is not applicable in cases where more than one solvent is present and / or it is not possible to distinguish a priori between solvent and solute. Further, the model describes the transport by means of phenomenological equations and considers the membrane as a black box without characterisation of membrane properties such as surface structure and surface charges. All these issues lead to few applications of the model in OSN.

2.3.1.2 Solution-diffusion (SD) mechanisms and their applications in OSN

Starting from the assumption that the overall driving force producing movement of a species i through a membrane is the gradient in its chemical potential across the membrane, as described by Equation (2.10).

$$J_i = -L_i \frac{d\mu_i}{dx} \quad \text{Equation (2.10)}$$

μ_i is the chemical potential and L_i is the coefficient of proportionality linking the chemical potential driving force and the flux. Although the chemical potential includes all forces such as concentration, temperature, pressure and electromotive force, in a membrane process, the driving force usually depends on concentration and pressure gradients, and therefore the chemical potential gradient can be written as Equation (2.11).

$$d\mu_i = RT d\ln(\gamma_i C_i) + v_i dP \quad \text{Equation (2.11)}$$

R and T are the ideal gas constant and the temperature, respectively. γ_i is the activity coefficient and v_i is the molar volume.

The solution-diffusion mechanism first introduced by Lonsdale et al. [56] in 1965 assumes that the pressure within a membrane is uniform, and that the chemical potential gradient across the membrane is entirely due to the concentration gradient, as shown in Figure 2.4. According to the solution-diffusion mechanism, in an ideal system, Equations (2.10) and (2.11) can be combined and reformed as Equation (2.12).

$$J_i = \frac{D_i K_i}{l} \left(C_{if} - C_{ip} e^{-\frac{v_i(P_f - P_p)}{RT}} \right) = P_i \left(C_{if} - C_{ip} e^{-\frac{v_i(P_f - P_p)}{RT}} \right) \quad \text{Equation (2.12)}$$

D_i is the diffusion coefficient of species i . K_i is the sorption coefficient, also known as partition coefficient of species i . l is the thickness of the membrane selective layer. Subscripts f and p refer to the feed and

permeate side, respectively. This equation is also known as a classical SD model, and can be used to describe the transport of both solute and solvent. P_i is the permeability coefficient of species i . When the applied transmembrane hydrostatic pressure ($P_f - P_p$) balances the osmotic pressure gradient ($\Delta\pi$), the solvent flux reaches zero ($J_j = 0$), thus

$$C_{jf} = C_{jp} e^{-\frac{v_j \Delta\pi}{RT}} \quad \text{Equation (2.13)}$$

Therefore the solvent flux can be reformed as Equation (2.14).

$$J_j = \frac{D_j K_j C_{jf}}{l} \left(1 - e^{-\frac{v_j (P_f - P_p - \Delta\pi)}{RT}} \right) \quad \text{Equation (2.14)}$$

If $\frac{v_i (P_f - P_p - \Delta\pi)}{RT}$ is small, Equation (2.14) can be simplified as Equation (2.15).

$$J_j = \frac{D_j K_j C_{jf}}{l} \frac{v_j}{RT} (P_f - P_p - \Delta\pi) = L_{j,simple} (P_f - P_p - \Delta\pi) \quad \text{Equation (2.15)}$$

$L_{j,simple}$ is the permeability coefficient of solvent j . Further, in a dilute system or a highly rejected system, the solute flux can also be simplified as Equation (2.16).

$$J_i = \frac{D_i K_i}{l} (C_{if} - C_{ip}) = P_{i,simple} (C_{if} - C_{ip}) \quad \text{Equation (2.16)}$$

Equations (2.15) and (2.16) are the two different mathematical formulas for a simplified SD model. $P_{i,simple}$ is the permeability coefficient of solute i in the simplified SD model.

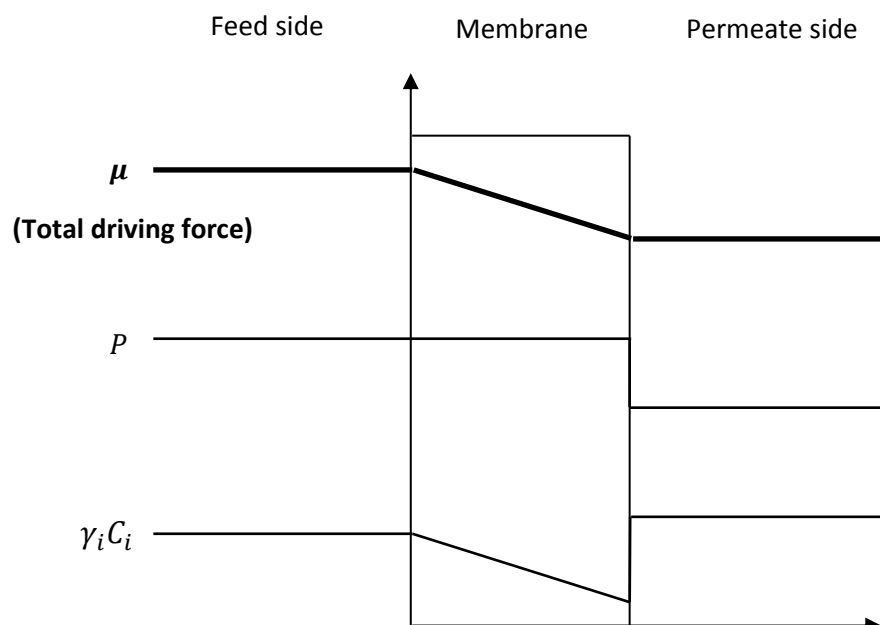


Figure 2.4: Schematic diagram of the solution-diffusion mechanism [56, 57].

The SD mechanism is usually adopted for transport through dense membranes where free volume elements are present as statistical fluctuations which appear and disappear at about the same time scale, as the motions of permeants through the membrane. These free volumes are different from pores which are usually fixed in time and space. According to the classical and simplified SD models, transport of permeants are independent with each other and separation is achieved due to the differing diffusivity of permeants in the membrane. Since the 1960s, these two SD mathematical models have been the most widely applied for the explanation of the transport in dialysis, reverse osmosis, gas permeation and pervaporation [57]. Recently, they have also been used to describe the molecular transport in OSN. White [37] applied the classical SD model (Equation (2.12)) to describe the transport of toluene solution containing six markers (straight chain alkanes: n-decane, n-hexadecane and n-docosane; a branched alkane: pristane; aromatic compounds: 1-methyl-naphthalene and 1-phenylundecane) through a PI (Lenzing P84) ISA membrane made in the laboratory. Since it is difficult to experimentally determine the values of the thickness of the membrane selective layer (l), the diffusion coefficient of species i (D_i) and the sorption coefficient of species i (K_i) individually, White calculated the permeability coefficient of each species i (P_i) which combined these three parameters, using the regression of the experimental transport

rate of each component. The calculated permeability coefficients were then used to predict the performance of the membranes under different operating conditions, and good agreement with the experiments was shown. Similarly, Han et al. [41] successfully applied the simplified SD model to predict the permeation of aqueous solutions of phenol and toluene through the polymeric MPF-50 membranes.

Furthermore, some studies have also shown that the SD models can be applied to predict the performance of PDMS membranes in various solvents where different degrees of membrane swelling occurred. Stafie et al. [42] characterised the permeation of two hexane solutions (sunflower oil / hexane and polyisobutylene (PIB) / hexane) through PDMS/PAN membranes under various feed concentrations and pressures. They found that the solvent flux correlated well with the ratio of swelling to viscosity and that the simplified SD model can describe the transport of hexane through the membranes well. Ben Soltane et al. [43] studied the effect of pressure on swelling of dense PDMS layers in three solvents (ethanol, toluene and n-heptane). These three solvents have distinct physical and chemical properties, leading to a wide range of swelling. They did not observe evidence of porous or pseudo porous structure in the swollen gel, and the existence of the concentration gradient was obvious. Further, the linearity of the solvent flux versus the applied pressure was shown, and the solvent diffusion coefficients calculated using Fick's law were consistent with those calculated from the SD mechanism. Based on these reasons, they believed that the SD model is capable of describing molecular transport through the PDMS membranes.

In the SD mathematical models discussed above (Equations (2.12), (2.15) and (2.16)), the activity coefficient of species i is assumed to be 1. However, this assumption may introduce considerable errors in some cases where the thermodynamic properties of the solutions are non-ideal, such as a solution of high-concentration tetraoctylammonium bromide (TOABr) in toluene [58]. Herein, in order to consider the thermodynamic non-ideality of the solutions, the classical SD model can be re-written as Equation (2.17) by introducing the ratio of activity coefficient of species i at permeate side to the one at feed side [38, 39].

$$J_i = P_i \left(C_{if} - \frac{\gamma_{ip}}{\gamma_{if}} C_{ip} e^{-\frac{v_i(P_f - P_p)}{RT}} \right) \quad \text{Equation (2.17)}$$

γ_i is the activity coefficient of species i . Silva et al. [38] applied Equation (2.17) to describe the permeation of the solvents (methanol, toluene, ethyl acetate and their mixtures) through StarMem® 122 membranes, using the permeability coefficient of each solvent obtained from the experimental flux in each pure solvent. The simulation showed good agreement with the experiments.

Concentration polarisation is a phenomenon which describes the accumulation of solutes adjacent to the membrane surface in the feed side when a solution flows across a semi-permeable membrane. It can increase the osmotic pressure gradient across the membrane and thus reduce the effective hydrostatic pressure driving force. This effect is usually more obvious in solutions with higher solute concentrations. As some examples in OSN, Peeva et al. [39] examined the performance of StarMem® 122 in two solutions (TOABr / toluene and docosane / toluene) upto 20 wt% concentration, and Silva et al. [40] performed the test for both StarMem® 122 and MPF-50 membranes in methanol with 5 – 30 wt% dimethyl methylsuccinate (DMMS). It was observed in both studies that increasing retentate flowrate can enhance the permeate flux, indicating the existence of concentration polarisation.

The concentration polarisation can be described mathematically using Equation (2.18), which is well-known as the film theory.

$$\frac{J_{tol}}{k_i} = \ln \left(\frac{C_{ifm} - C_{ip}}{C_{if} - C_{ip}} \right) \quad \text{Equation (2.18)}$$

J_{tol} is the total flux of the solution and k_i is the mass transfer coefficient of species i . Subscript fm refers to the solution phase adjacent to the membrane surface in the feed side. The effect of concentration

polarisation can be considered in the classical SD model by coupling the film theory, as shown in Equation (2.19). Peeva et al. [39] and Silva et al. [40] successfully used this equation to predict their experiments.

$$J_i = P_i \left(C_{ifm} - \frac{\gamma_{ip}}{\gamma_{ifm}} C_{ip} e^{-\frac{v_i(P_f - P_p)}{RT}} \right) \quad \text{Equation (2.19)}$$

Paul [59] pointed out that the classical and simplified SD models may fail in describing separation in OSN, as they are not capable of accounting for any kind of coupling between solute and solvent fluxes. Further, in the simplified SD model, the linearity of the flux against the pressure is expected, although this disagrees with the experimental observations in some studies [39, 40, 59]. In addition, the simplified SD model is not capable of describing the negative rejection which was observed in some studies [60, 61]. In order to overcome these limitations of the classical and simplified SD models, Paul [59] adapted the Maxwell-Stefan equations to consider potential frictional or convective coupling effects between solute and solvent within the membrane based on the solution-diffusion mechanism. This model is known as Maxwell-Stefan model and can be mathematically described as:

$$-\sum_{j \neq i} \frac{x_i x_j}{D_{ij}^{MS}} (u_i - u_j) = x_i \nabla \ln a_{i(m)} \quad \text{Equation (2.20)}$$

D_{ij}^{MS} is the multicomponent diffusion coefficient. x_i is the molar fraction of species i in the mixture and u_i is the velocity of species i relative to stationary coordinates. $a_{i(m)}$ is the activity of species i in the solvent-solute-membrane mixture.

Gevers et al. [44] applied the Maxwell-Stefan model to explain the transport of dye solutes through dense silicone OSN membranes in alcohols, and good agreement was shown. In the study, the molar volume of the solutes played an important role. Specifically, for the solutes with small molar volumes, the convective flux had an important contribution, especially when the available space between polymer chains was

increased due to swelling, while for solutes with large molar volume, the diffusive flux was a dominant contribution. Hesse et al. [45] developed a predictive model based on Maxwell-Stefan equations, accounting for the diffusivity and solubility of the organic solvents in the dense active separation layer and swelling. This model was used to predict the flux of pure organic solvents (ethyl acetate, isopropanol, toluene and ethanol) and their mixtures through a commercial PI-based StarMem® 240 membrane, and good agreement with the experimental data was shown.

2.3.1.3 Pore-flow (PF) mechanisms and their applications in OSN

Also starting from the assumption that the overall driving force producing movement of a species i through a membrane is the gradient in its chemical potential across the membrane, the PF mechanism expresses the chemical potential as a pressure gradient in physically distinguishable pores with the assumption of uniform concentration within a membrane, as shown in Figure 2.5. Transport of molecules through a membrane is via permeation pathways (pores) of which the diameter is larger than the solute and solvent molecular diameters [55].

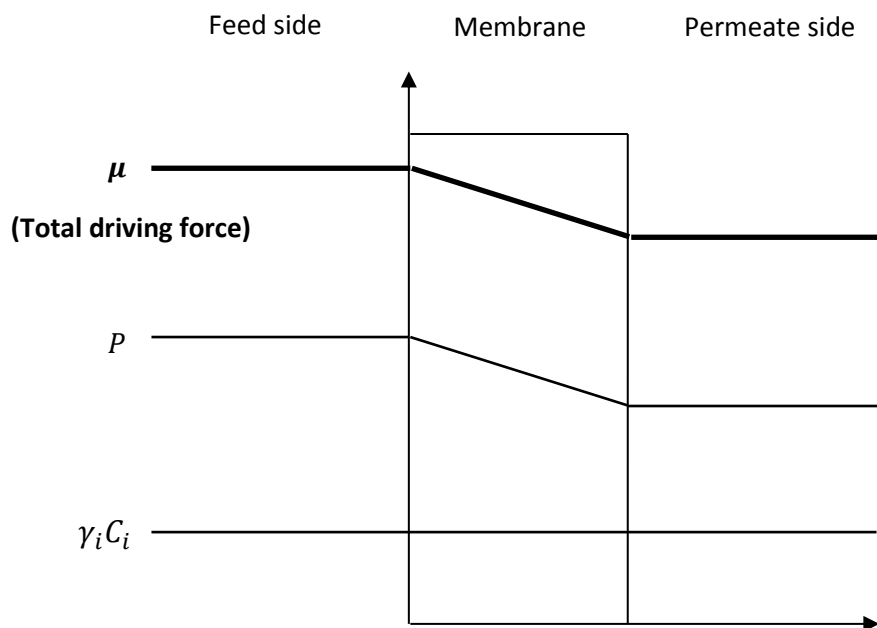


Figure 2.5: Schematic diagram of the pore-flow mechanism [34, 39].

In the absence of a concentration gradient, the transport through porous membranes can be described by Darcy's law which is expressed as Equation (2.21).

$$J_{tol} = k_D \frac{P_f - P_p}{l} \quad \text{Equation (2.21)}$$

k_D is the permeability coefficient which is a function of membrane structural factors, such as membrane pore size, surface porosity and tortuosity. The well-known Hagen–Poiseuille (HP) model, derived from Darcy's law, can be generally used to describe the solvent transport through a porous membrane, as shown in Equation (2.22).

$$J_{tol} = \frac{\varepsilon r_p^2}{8l\tau} \frac{P_f - P_p}{\eta} = K_{HP} \frac{P_f - P_p}{\eta} \quad \text{Equation (2.22)}$$

K_{HP} is the dimensionless coefficient in the HP model, including four membrane characteristics: the membrane porosity, ε , the membrane tortuosity, τ , the membrane pore radius, r_p and the membrane thickness, l . The solvent property is only considered using the dynamic viscosity, η . In different solvents, the characteristics of the same membrane may change due to different degrees of membrane swelling, making the prediction of solvent transport more complicated [65].

For the solute transport, many empirical mathematical models were developed. Based on both the friction model [66, 67] and Haberman and Sayre's expression for the frictional drag force, Verniory et al. [68] gave the expression of the transport for an ideal solute (known as the Verniory model):

$$J_i = D_i \cdot F_2(\lambda) \cdot S_D \cdot \frac{A_k}{\Delta X} \cdot \Delta C_i + J_{tol} \cdot \overline{C_i} \cdot F_1(\lambda) \cdot S_C \quad \text{Equation (2.23)}$$

where

$$\lambda = \frac{r_s}{r_p} \quad \text{Equation (2.24)}$$

$$S_D = (1 - \lambda)^2 \quad \text{Equation (2.25)}$$

$$S_C = 2(1 - \lambda)^2 - (1 - \lambda)^4 \quad \text{Equation (2.26)}$$

$$F_1(\lambda) = \frac{1 - \frac{2}{3}\lambda^2 - 0.20217\lambda^5}{1 - 0.75857\lambda^5} \quad \text{Equation (2.27)}$$

$$F_2(\lambda) = \frac{1 - 2.105\lambda + 2.0865\lambda^3 - 1.7068\lambda^5 + 0.72603\lambda^6}{1 - 0.75857\lambda^5} \quad \text{Equation (2.28)}$$

A_k is the ratio of cross-section pore area to effective membrane area and ΔX is the pore length. D_i is the diffusivity of species i . S_D and S_C are the steric hindrance factors for diffusion and convection forces, respectively. F_1 and F_2 are the wall correction factors. Comparing Equation (2.23) with the Kedem-Katchalsky model (Equation (2.5)), the reflection coefficient of solute can be expressed as Equation (2.29):

$$\sigma_s = 1 - F_1(\lambda) \cdot S_C \quad \text{Equation (2.29)}$$

Nakao and Kimura [69] eliminated the wall correction factors and gave another expression for the reflection coefficient, as shown in Equation (2.30), which is known as the steric hindrance pore (SHP) model. The pore size is assumed to be uniform in this model.

$$\sigma_s = 1 - S_C \cdot \left(1 + \frac{16}{9}\lambda^2\right) \quad \text{Equation (2.30)}$$

Ferry [70] proposed another PF model, known as the Ferry model. The Ferry model assumes the pores to be uniform and cylindrical, and the velocity in the pore has a parabolic profile. The reflection coefficient is expressed as:

$$\sigma_s = 1 - 2(1 - \lambda)^2 + (1 - \lambda)^4 \quad \text{Equation (2.31)}$$

In the empirical models discussed above, the pore size is assumed to be uniform. Differently, Van Der Bruggen et al. [72] considered the log-normal pore size distribution and proposed a so-called log-normal model. According to this model, the reflection coefficient curve can be expressed as:

$$\sigma_s = \int_0^{r_s} \frac{1}{S_p \sqrt{2\pi}} \frac{1}{r} \exp\left(-\frac{(\ln r - \ln \bar{r}_p)^2}{2S_p^2}\right) dr \quad \text{Equation (2.32)}$$

S_p is the standard deviation of the pore size distribution.

Matsuura and Sourirajan [75] considered the interaction between solute and membrane material at the solution-membrane interface using electrostatic or Lennard-Jones-type surface potential functions and developed the surface force pore flow (SF-PF) model. This model can be expressed as Equation (2.33).

$$J_i = -\frac{RT}{\chi_{iv} b} \frac{dC_i}{dx} + \frac{C_i J_{tol}}{b} \quad \text{Equation (2.33)}$$

where

$$b = \frac{\chi_{iv} + \chi_{im}}{\chi_{iv}} \quad \text{Equation (2.34)}$$

χ_{iv} and χ_{im} are the friction coefficients between solute and solvent, and between solute and membrane, respectively. They are a function of the diffusion coefficient of the solute in the solvent, and the solute in the membrane material. However, Mehdizadeh and Dickson [78] claimed that in the SF-PF model, the form of the material balance is incorrect and the potential function in the pore is inconsistent with the cylindrical

pore geometry. They revised the model based on the same physical precepts but the corrected mass balance, and the revised model is known as the modified SF-PF model.

The PF models require the specification of which species is the solute and which species is the solvent. In the case of n solutes in the mixture, the PF models can be extended to calculate the local solute flux for each species (J_i , for $i = 1 - n$), but it is not clear how to extend the models in the case of solvent mixtures or how to use the models when it is not possible to a priori distinguish between solute and solvent. The PF models were proposed in the nineteenth century and have been widely accepted in the description of transport in ultrafiltration and microfiltration, since they are close to normal physical experience. Recently, some studies have also extended them from aqueous applications to OSN.

Van Der Bruggen and Vandecasteele [46] predicted the rejection of organic molecules through a membrane using the effective size of the organic molecules (mathematically related to the molecular weights) based on the log-normal model. In this model, the pore size distribution in the membrane, the reflection coefficient distribution and the diffusion parameter were determined from regression of the experimental flux and rejection based on both the log-normal model and the Stokes-Einstein's law. The model was verified satisfactorily for three commercial membranes (NF 70, UTC-20 and NTR 7450). Gibbins et al. [48] investigated the solvent flux decline and the membrane separation properties in solutions of quaternary alkyl ammonium bromide salts ($MW = 322 - 547 \text{ g mol}^{-1}$) in methanol using three commercial membranes (StarMem® 122, MPF-50 and Desal DL), and estimated the size of the pores in the membranes using three different PF models (the SHP model, the Ferry model and the Verniory model). Bhanushali et al. [49] experimentally investigated the performance of six different membranes (PDMS and PA – based membranes) in both polar and non-polar solvents (alcohols and alkanes) with organic dyes and triglycerides as solutes, and applied the existing membrane transport models (the SD model, the Spiegler-Kedem model and the SF-PF model) to describe the data. Interestingly, they found that the rejection of Sudan IV dye was about 25% in n-hexane and about -10% in methanol for the PDMS-based membrane, and about 86% in

methanol and about 43 % in n-hexane for the PA-based membrane. Based on these data, they concluded that solute rejection is strongly affected by the solute-solvent-membrane coupling effects, thus the SD model is not adequate to describe the solute transport. The Spiegler-Kedem model demonstrated the importance of the convective flow on the overall transport especially when the solute MW was small, and the SF-PF model accounts for solute-membrane interactions via a potential function and is capable of describing the negative rejection.

Geens et al. [47] compared the SHP model, the Ferry model and the Verniory model with the log-normal model, using the experimental performance of different hydrophilic and hydrophobic membranes (PDMS, PA and TiO₂) in methanol, ethanol, acetone, ethyl acetate and n-hexane with various reference solutes. The better fit of the log-normal model with the experimental data suggests the non-uniformity of the pores in the membranes. Besides, the membrane characteristics (pore size and pore size distribution) obtained from the regression suggest their high dependency on solvents. Robinson et al. [50] suggested that the permeation of alkanes, aromatic solvents and alcohols through a PDMS based membrane can be successfully interpreted using the HP equation. At pressures above 3 bar, solvent transport can be predominantly described using a hydraulic mechanism, whereas below this threshold level, a second mechanism including the effects of both sorption and diffusion is more apparent. The non-separation of solvent mixtures passing through the membrane and a dependency on viscosity and membrane thickness support a hydraulic mechanism. In addition, the HP proportionality constant is correlated with the Hildebrand solubility parameter of the solvent, proving the importance of swelling effects. Recently, Leitner et al. [51] gave the better description of the transport through a dense layer PDMS membrane (usually described by the SD model) using the HP equation and several pressures and solvents were studied in order to research various degrees of swelling and compaction. In addition, the profile of the flux over the pressure is linearized by correlating the membrane thickness with the pressure, proving the suitability of the hydraulic mechanism for this study.

2.3.1.4 Solution-diffusion with imperfections (SDI) mechanisms and their applications in OSN

The SDI mechanism was developed about 50 years ago by Sherwood et al. [86] who claimed that it is important to consider the occurrence of both viscous flow and diffusion flow due to the existing of imperfections in a membrane. Therefore they extended the classical SD model by introducing two parallel transport paths through a membrane matrix. Specifically, the SD mechanism is used to describe the transport through dense materials while in the imperfections the species are convectively transported without change of concentration (the same as PF mechanism). This model can be mathematically described as Equations (2.35) and (2.36).

$$J_{tot} = L_V(\Delta P - \Delta\pi) + L_i\Delta P \quad \text{Equation (2.35)}$$

$$J_i = P_i\Delta C_i + L_iC_F\Delta P \quad \text{Equation (2.36)}$$

L_V and L_i are the partial mechanical permeability coefficients of the matrix and imperfections, respectively.

P_i is the partial diffusional permeability coefficient of the matrix.

Applications of the solution-diffusion with imperfection models in OSN are rare. Dijkstra and Ebert [52] applied both the Maxwell-Stefan model and the SDI model to describe the permeation of various mixtures of pentane-decane and pentane-dodecane through dense PDMS membranes. Although the SDI model gave good predictions, they claimed that the Maxwell-Stefan model is better since the estimated model parameters from the Maxwell-Stefan model are more realistic.

2.3.1.5 Summary

Various membrane transport mechanisms and the corresponding mathematical models have been reported in the literature and their potential applications in OSN have been presented [13]. Importantly, Marchetti and Livingston [61] conducted a systematic comparison of the different membrane transport

models (the IT model, the SD model, the PF model and the SDI model), using the extensive experimental data for different commercial and non-commercial membranes in various solvents. The membranes had different MWCOs and the solvents covered a wide range of physico-chemical properties such as viscosity, polarity and solubility. They pointed out that the existing membrane transport models are sufficient for describing molecular transport in current OSN membranes and gave a criterion for selecting a suitable membrane transport model for a specific OSN application based on membrane materials. Specifically, the SD models gave better descriptions for flexible-chain glassy membranes while the PF models are more suitable for glassy membranes. Among the SD models, both the classical SD and the Maxwell-Stefan models gave good descriptions of the molecular transport through flexible-chain glassy membranes. Although the Maxwell-Stefan model has slightly higher accuracy, it is more complex in terms of model parameter regression / estimation. In addition, both the Maxwell-Stefan model and the classical SD model were used to predict the performance of a concentration process and interestingly, no significant difference was observed. Therefore they concluded that the classical SD model is sufficient to describe the performance of OSN processes with flexible-chain glassy membranes. In this research, the silicone coated membranes (flexible-chain glassy membranes) were used, therefore the classical SD model was chosen to describe the membrane transport.

2.3.2 Fluid dynamics and mass transfer characteristics in spiral-wound membrane modules

In spiral-wound membrane modules, the fluid dynamics and mass transfer characteristics are key for the performance of the modules. Specifically, the fluid dynamics characteristics determine the pressure drop through the module channels which affects the effective pressure driving force (the transmembrane pressure), and the mass transfer characteristics determine the concentration polarisation which affects both module flux and rejection. In the module channels, the fluid dynamics and mass transfer characteristics are different from that well known in an empty rectangular or cylindrical channel, due to the spacers which introduce vortices and energy dissipation and add complexity. Over the past few decades, many researchers have studied fluid dynamics and mass transfer through planar, spacer-filled channels,

mimicking of module channels, in aqueous solutions. As a summary, three main methods have been used to determine the mass transfer coefficient in the literature [88 – 103]: (i) direct measurements, which used optical or electrochemical methods; (ii) indirect measurements, which were based on regression of membrane performance data using a combination of the film theory and membrane transport models; and (iii) computational fluid dynamics (CFD) simulations, which were based on a priori simulation of the module geometry. The pressure drop characteristics were usually determined either from direct measurements, using accurate pressure gauges, or via CFD simulations [88, 91 – 95, 102].

Among the direct measurement approaches, Johnson [89] applied an interferometer with a helium-neon laser as a light source to measure concentration polarisation in a reverse osmosis system. However, this method introduced a significant error due to the deflection of the light from a solute even in dilute conditions. Balster et al. [90] studied the effects of various single and multi-layer spacers on mass transfer using the limiting current technique. They concluded that the multi-layer spacer configurations exhibited significant mass transfer enhancement with respect to single-layer ones. However, in their work, the flow passed along impermeable channel walls, which are obviously different from the semi-permeable membrane walls present in a membrane module. Schock and Miquel [88] measured the pressure drop through various feed and permeate spacer filled channels. A friction coefficient correlation was used to fit their experimental data, in the form of Equation (2.37):

$$f = \frac{2\Delta P d_h}{\rho u^2 L} = a \left(\frac{d_h \rho u}{\eta} \right)^b = a Re^b \quad \text{Equation (2.37)}$$

f is the friction coefficient and ΔP is the pressure drop through the channel. d_h is the hydraulic diameter of the channel, L is the length of the channel, ρ is the density of the solution, u is the velocity of the flow along the channel, η is the dynamic viscosity of the solution and Re is the Reynolds number. a and b are the coefficient and the exponent of Reynolds number in the friction coefficient correlation, respectively. In Schock and Miquel's work, the spacer geometry was measured using a light microscope; however the

authors pointed out that this might not be a very accurate technique to obtain the characteristic dimensions of permeate spacers, due to their complicated geometry. They found that the geometry of the feed spacer had little effect on the friction coefficient, while the geometry of the permeate spacer showed more significant effects. Kuroda et al. [91], Da Costa et al. [92] and Schwinge et al. [93] also studied the effects of spacer geometry on the friction coefficient. Various types of spacers were considered in their work and a number of experimentally measured pressure drop data were reported. The significant effects of the spacer geometry on pressure drop performance were observed.

Among the indirect measurement approaches, Schock and Miquel [88] performed regression of flat sheet membrane performance data to determine the mass transfer coefficient in planar, feed spacer filled channels using the combination of film theory and an empirical membrane transport model. This empirical transport model assumes that the permeate flux is linearly dependent on the difference between the applied pressure and the osmotic pressure. The authors used a dimensionless correlation to describe the mass transfer coefficient, in the form of Equation (2.38):

$$Sh = \frac{k d_h}{D} = \alpha Re^\beta Sc^\lambda = \alpha \left(\frac{d_h \rho u}{\mu} \right)^\beta \left(\frac{\mu}{\rho D} \right)^\lambda \quad \text{Equation (2.38)}$$

Sh and Sc are the dimensionless Sherwood and Schmidt numbers, respectively. α , β and λ are the coefficient and the exponents in the Sherwood correlation equation. k is the mass transfer coefficient and D is the diffusivity of a solute in a solvent. Four types of commercial feed spacers were studied in their work; interestingly, no effect of the spacer geometry on the mass transfer coefficient was observed. A similar methodology was used by Da Costa et al. [92] and Schwinge et al. [93], who on the other hand, found that the spacer geometry does affect the mass transfer coefficient in spiral-wound membrane modules. Interestingly, their correlations [92, 93] for the same spacers showed good agreement.

Finally, among the CFD studies on the mass transfer coefficient, Da Costa et al. [94] and Karode and Kumar [95] performed 2 dimensional CFD simulations to visualize the fluid flow structure through various spacer filled flat channels. They found that the flow path was affected by a combination of flow attack angle, filament size, mesh size and angle between crossing filaments. In these two studies, the friction coefficient correlations for the same spacers showed good agreement. Li et al. [96 – 98] performed 3 dimensional CFD simulations to study flow characteristics and mass transfer in spacer-filled channels and the results were compared with their experimental data. Good agreement was reported and various correlations in the form of Equation (2.38) were presented. Fimbire-Weihs and Wiley [99] presented both 2 and 3 dimensional CFD simulations to study mass transfer in spacer filled channels, positioned at 45° and 90°, with a single Schmidt number ($Sc = 600$). The authors reported that the exponent of Reynolds number in the Sherwood correlation, represented in the form of Equation (2.38), is 0.591. Koutsou et al. [100] reported extensive mass transfer coefficient data for ten types of spacers and discussed the effect of Schmidt number on the mass transfer coefficient using CFD simulations. Furthermore, various Sherwood number correlations were reported based on average mass transfer coefficients and good agreement with Li et al.'s work [98] was observed. Kostoglou and Karabelas [101] developed a comprehensive model which incorporates small scale CFD results on the retentate side and accounts for permeate variables as a step forward to predict the performance of spiral-wound membrane modules in desalination. Karabelas et al. [102] performed a parametric study on the performance of spiral-wound membrane modules in steady state mode in desalination using an advanced simulator, considering pressure drops and mass transfer characteristics obtained from CFD, and reported on the importance of spacer geometry and membrane envelope width on module performance. CFD studies help to understand and visualise the flow path in spacer-filled channels and to give knowledge on the optimisation of spacer geometry. However, most of these studies were made using simple-geometry spacers with regular filament shapes such as ladder spacers with cylindrical filaments. Many spacers used in commercial modules have more complex geometry, such as cylindrical filaments with some cut-offs and with woven multi-layer structure. Besides, information about the spacer geometry in commercial modules is usually confidential and therefore unavailable for end users without performing a module autopsy. All these factors make CFD simulations more complicated to use.

Overall, it is clear that the spacer geometry significantly affects the fluid dynamics and mass transfer characteristics in the spacer filled channels of SWMMs and many correlations for describing the fluid dynamics and mass transfer characteristics in the form of Equations (2.37) and (2.38) were reported in the literature. However, no work so far has numerically related the spacer geometry with the values of the coefficients and the exponents in the friction coefficient and Sherwood number correlations. In addition, all the correlations reported in the literature were derived in aqueous solutions, and may be not suitable in OSN applications. This is since in OSN, the variety of solvents and solutes results in a broad range of possible Reynolds and Schmidt numbers, making the fluid dynamics and mass transfer in SWMMs different and more complicated compared to aqueous applications. From a design and prediction point of view, there are still challenges to select / generate suitable correlations for describing the fluid dynamics and mass transfer characteristics in SWMMs for OSN applications.

2.3.3 OSN process models

A reliable process model is crucial for developing an OSN process. So far several process models have been proposed for OSN processes. Sereewatthanawut et al. [26], Peshev et al. [103] and Vanneste et al. [104] proposed a process model for a diafiltration process and a membrane cascade based on the mass balance derived with the assumptions of well-mixed solutions in a feed tank and negligible time consumed for retentate circulation, and they also assumed constant flux and rejection over the process. Under these assumptions, the process models showed good agreement with the experimental data. However, these models were not capable of predicting the performance of other applications. This was due to the fact that they used empirical, non-predictive membrane transport models and assumed constant flux and rejection over the process, which has been shown to be unrealistic in many cases [39]. Recently, Schmidt et al. [105] claimed that design methods for integrating OSN in chemical production processes in contrast to well-established design approaches for conventional unit operations are fewer and development of a suitable process design method is one of the challenges for improving OSN technology. They established a four-step general design workflow for OSN processes, including (i) determination of minimum separation targets; (ii)

preselection of membranes and solvents based on molecular weight and the membrane rejection maps and membrane modelling maps previously proposed by the same group [106, 107]; (iii) experimental validation of the conditions optimised from (ii); and (iv) optimisation of the process based on modelling and detailed economic data. This four-step design workflow is demonstrated on a case study of industrial importance which is the recycling of homogeneous catalysts. In the same year, Micovic et al. [108] presented a similar four-step design approach for a hybrid separation combining distillation and OSN. This method was applied to investigate separation of heavy boiler (hexacosane, 5 %) from low- and middle-boiler (decane, 70 % and dodecanal, 25 %) in a wide boiling mixture from hydroformylation. Although these studies make an important contribution to process design for OSN, they ignore the effects of the fluid dynamics and mass transfer characteristics on the module performance and assume identical performance between membrane and module. This simplified assumption might introduce significant deviation in the industrial applications.

The availability of all required thermodynamic and physical properties of the solutions of interest, as a function of the operating conditions, is crucial for a process model. However, this has not been considered in the process models above [26, 103 – 105, 108]. Considering that the collection of thermodynamic and physical data for all the possible solute/solvent combinations by experiments would be prohibitively time consuming, it is useful to rely on a simulation tool to predict the values of these properties. Peshev and Livingston [30] recently proposed a tool, “OSN Designer”, which makes OSN unit operations available in process modelling environments such as Aspen Plus, HYSYS and ProSim Plus, to streamline OSN process design. The thermodynamic and physical properties of the solutions were thus obtained from the Aspen Properties Database or estimated using built-in models in the process modelling environment and applied in the OSN unit operations. This tool was validated using published experimental data under steady-state and batch conditions. However, the effects of the fluid dynamics and mass transfer characteristics on module performance were not considered, and so the OSN Designer is not able to predict the performance of a process using SWMMs.

Chapter 3

Performance of spiral-wound membrane modules in OSN – fluid dynamics and mass transfer characteristics

3.1 Introduction

The development of a membrane process, such as OSN, usually involves several stages, starting from feasibility tests at laboratory scale, passing through pilot plant tests and finishing with large industrial scale processes, and the availability of a reliable simulation model could make the transition between these stages smoother and easier. Three scales can be distinguished within the general process modelling framework: membrane transport at molecular scale, fluid dynamics and mass transfer in membrane modules and performance at process scale [30]. Many studies on the transport mechanism through OSN membranes have been published; however, most of these studies were made using flat sheet membranes and at the level of molecular transport. Only few studies [13, 104, 105] described the performance of OSN processes with spiral-wound membrane modules using some simple, non-predictive membrane transport models; however, the effects of the modules at process level were not explored. In the literature, there has been only one study which investigated fluid dynamics and mass transfer characteristics in a spiral-wound membrane module for OSN. In that study, Silva et al. [27] reported the experimental and simulated performance of a 2.5"x40" spiral-wound StarMem® 122 membrane module in 0 – 20 wt% solutions of

TOABr in toluene using a steady-state approach. In their modelling, two solution-diffusion based models were used and the corresponding model parameters were determined from flat sheet data; the former approach was a simple model, which assumed uniform pressure and concentration in both feed and permeate sides, while the latter was a complex model, which considered spatial concentration, velocity and pressure gradients. Although both models showed good agreement with the experimental data for the system under study, the authors pointed out that the complex model is more appropriate when the assumptions of both pressure and mass transfer coefficient constancy are not acceptable. The pressure drop and mass transfer correlations used in their study were adapted from Schock and Miquel's work [88]. Finally, in their study, the effects of membrane type and module size on the overall process performance were not explored.

It is clear that the spacer geometry significantly affects the fluid dynamics and mass transfer characteristics in the spacer-filled channels of spiral-wound membrane modules. Accordingly, many correlations in the form of Equations (2.37) and (2.38) were reported. However, all these correlations were derived in aqueous solutions and no work so far has numerically related the spacer geometry with the values of the coefficients and the exponents in the friction coefficient and Sherwood number correlations. In comparison to desalination, the variety of solvents and solutes in OSN makes fluid dynamics and mass transfer in SWMMs even more complicated due to a broad range of possible Reynolds and Schmidt numbers. In addition, the spacer geometry in commercial SWMMs is usually confidential and not available for end users. This fact makes the selection of suitable correlations even impossible. Therefore, there are still challenges to select / generate suitable correlations for describing the fluid dynamics and mass transfer characteristics in SWMMs for OSN applications.

In this chapter, the performance of four SWMMs tested in 0 – 20 wt% solutions of SoA in EA under various pressures and retentate flowrates is presented and discussed. These modules were made with two different membranes (a commercial membrane, PuraMem® S600, and a development product, Lab-1, from

EMET) and covered three module sizes (1.8"x12", 2.5"x40" and 4.0"x40"). All modules had the same feed and permeate spacers (referred to as EMET-F3 and EMET-P1, respectively). The classical SD model was applied to describe the transport of solute and solvent through the membrane and regress the unknown model parameters from flat sheet performance data. Correlations for characterising the fluid dynamics and mass transfer in the SWMMs, as well as the parameters describing the geometry of both the feed and permeate channels, were determined by regression of experimental data of a 1.8"x12" PuraMem® S600 membrane module. The classical SD model, combined with the film theory, was then successfully applied to predict the performance of three further modules of larger size (such as the 2.5"x40" and 4.0"x40" module sizes) and/or made with a different membrane material (such as Lab-1). The procedure developed in this chapter can predict the performance of a specific module by obtaining a limited number of experimental data for flat sheets and a 1.8"x12" spiral-wound membrane module only (necessary to obtain the fitting parameters characteristic of the membrane and the module). Furthermore, with this procedure, it is not necessary to know a priori the spacer geometry, because the necessary information about the spacer geometry will be also obtained by regression of few experimental data.

3.2 Materials and methods

3.2.1 Materials

Analytical grade EA was purchased from Tennants Distribution Limited, UK. SoA (>97% purity) was purchased from Sigma Aldrich Limited, UK. EA was chosen as a solvent because it is commonly used in industry. SoA was chosen as a solute, for its good solubility in EA and its low price, which are important factors when carrying out experiments at a large scale and using highly concentrated solutions, such as the case in this study.

Flat sheets of PuraMem® S600 (PM S600, A4 size) were provided by EMET. EMET also provided flat sheets of a development rubbery membrane, referred to as Lab-1 in this study. As shown in Figure 3.1, the thickness of the top silicon layer of the Lab-1 membrane is about 100 nm.

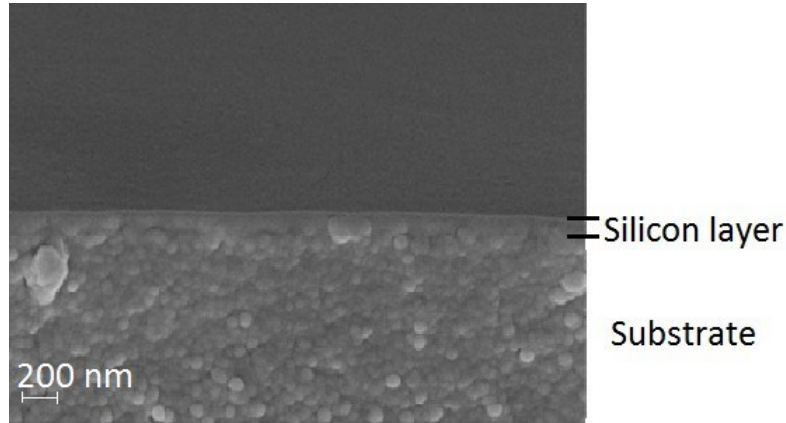


Figure 3.1: Scanning electron microscope image of the cross section of Lab-1 membrane.

Four SWMMs were also provided by EMET, three of them made of PM S600 membrane and the other one made of Lab-1 membrane. All modules had the same feed and permeate spacers (referred to as EMET-F3 and EMET-P1, respectively). Both the length and width of the permeate channel (L_p and W_p , respectively) are about 70 mm shorter than the feed channel due to the presence of glue lines on the permeate side. The details about the configuration of these four modules are summarised in Table 3.1.

Table 3.1: Configuration of the four SWMMs used in Chapter 3. All information is provided by the supplier

Module Code	Module Size	Membrane Type	Membrane Area (m ²)	Number of Leaves	Module Body Length (mm)
SWMM-1	1.8"x 12"	PM S600	0.14	1	175
SWMM-2	2.5"x40"	PM S600	1.74	2	886
SWMM-3	4.0"x40"	PM S600	5.19	4	886
SWMM-4	2.5"x40"	Lab-1	1.87	2	886

3.2.2 Methods

3.2.2.1 Performance of flat sheet membranes

Solvent flux and solute rejection of both flat sheet PM S600 and Lab-1 membranes were measured in a 4-cell cross-flow filtration system, as shown in Figure 3.2(a). The flat sheet membranes were initially conditioned at 5 bar for 5 – 7 hours using pure EA to remove the preservatives inside the membranes. The membranes were then tested in pure EA, followed by 1 g L⁻¹ SoA in EA solution at various feed pressures (from 5 to 30 bar in increasing order 5 → 10 → 20 → 30, and then in decreasing order back to 5 bar) with a retentate flowrate of 80 L h⁻¹ (obtained with a Hydra-Cell D3 pump). The volume of the feed solution was around 3.5 L. This pressurisation and depressurisation test was repeated three times for each membrane. Four discs of the same membranes were tested simultaneously in the cross-flow equipment. In total, two test runs were performed for each type of membrane. The permeate flux was measured every hour until the flux had remained stable for 3 hours under each test condition. The average of the last three measurements was recorded as the membrane flux. Permeate and retentate samples were taken at 3 different time points with one hour interval after the steady-state flux condition was reached. The average of these three rejections was recorded as the membrane rejection.

3.2.2.2 Performance of spiral-wound membrane modules

All the SWMMs were initially conditioned at 5 bar for 5 – 7 hours using pure EA to remove the preservatives from the membrane. These modules were then tested in pure EA at 30 °C and various feed pressures (from 10 to 30 bar in increasing order: 10 → 20 → 30). After that, the modules were tested in solutions of SoA in EA with different concentrations (from low concentration to high concentration in increasing order: 1 wt% → 10 wt% → 20 wt%). In each solution, the modules were tested at various feed pressures (10, 20 and 30 bar) with 3 or 4 different retentate flowrates. The permeate flux was measured every hour until the flux had remained stable for 3 hours under each test condition. The average of the last three measurements was recorded as the module flux. Permeate and retentate samples were taken at 3 different time points with one hour interval after the steady-state flux condition was reached. The average

of these three rejections was recorded as the module rejection. To allow for suitable flowrates in each module size, different test equipment was used for the different modules. The smallest SWMM-1 module (1.8"x12") and the intermediate SWMM-2 and SWMM-4 modules (2.5"x40") were tested in a system provided with a single diaphragm pump, as shown in Figure 3.2(b), whereas the largest SWMM-3 module (4.0"x40") was tested in a two-pump system, as schematically shown in Figure 3.2(c). Specifically, the smallest SWMM-1 module was tested using the same diaphragm pump as in the flat sheet membrane test equipment (Hydra-Cell D3), where the flowrate was varied from 80 to 240 L h⁻¹. Differently, the SWMM-2 and SWMM-4 modules were tested using a more powerful diaphragm pump, capable of controlling the flowrate from 200 to 1000 L h⁻¹ (Hydra-Cell D10). Finally, in order to supply sufficient linear feed velocity in the test of the 4.0"x40" SWMM-3 module, a circulation pump (Peripheral-Pump HMM125) was added (see Figure 3.2(c)). After the Flow Indicator 1, a fraction of the retentate circulates through the module with a high flowrate, forming an inner circulation loop (Heat Exchanger → Circulation Pump 1 → Pressure Indicator 1 → Module Housing → Pressure Indicator 2 → Flow Indicator 1 → Heat Exchanger). The remaining fraction of the retentate flows back through the back pressure valve to the feed tank (recycle fraction). The feed flowrate through the module in the inner circulation loop was controlled between 2,000 and 3,000 L h⁻¹ and the fluid flowrate after the back pressure valve was controlled to be around 75 L h⁻¹, 155 L h⁻¹ and 230 L h⁻¹ at the feed pressure of 10 bar, 20 bar and 30 bar, respectively. The volume of the feed solution in the tests for the 1.8", 2.5" and 4.0" modules was around 3.5 L, 30 L and 40 L, respectively. In all the tests, the pressure drop through the empty housing was measured before the installation of the module.

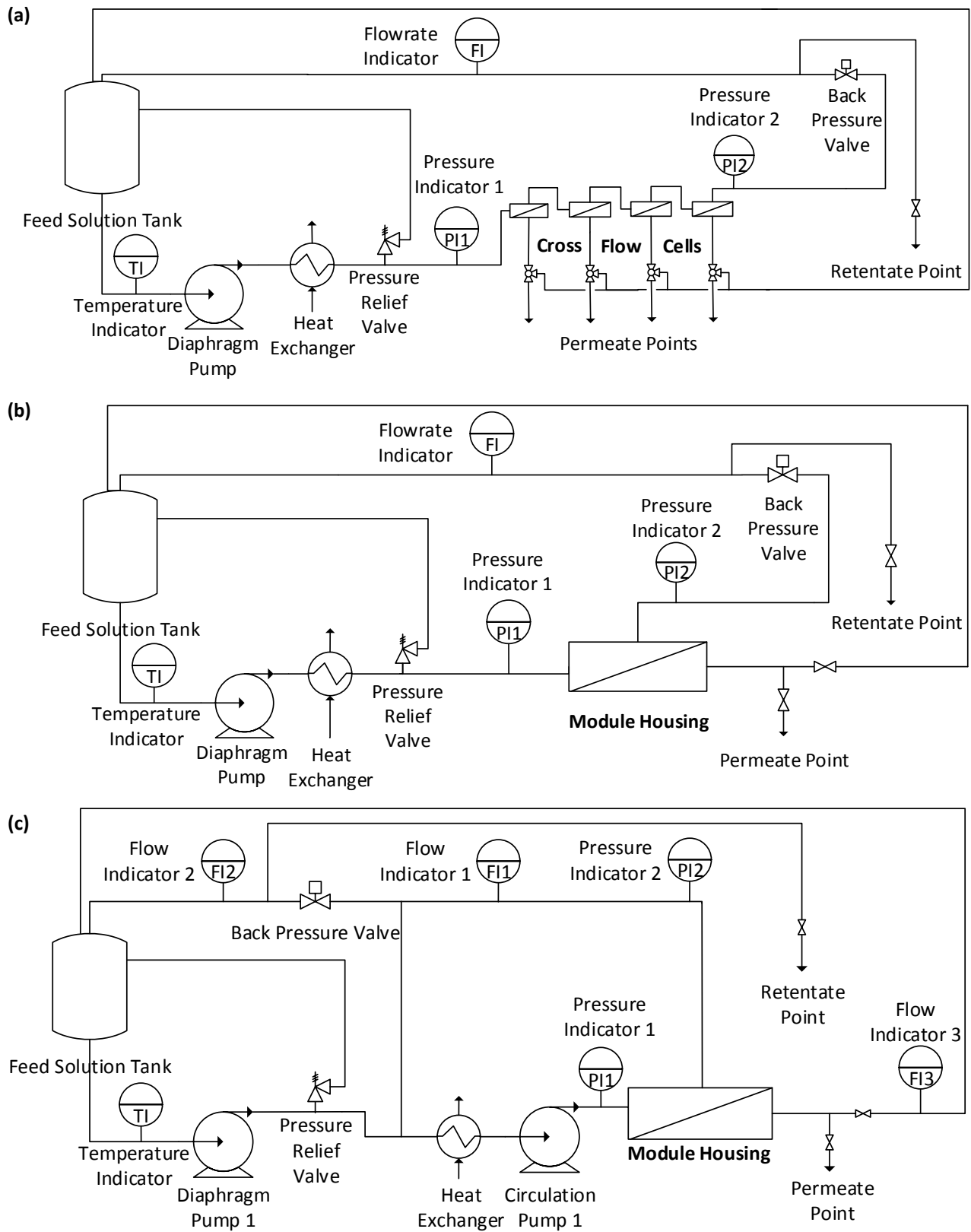


Figure 3.2: Schematic diagrams of the module testing equipment: (a) single-pump configuration for the flat sheet membrane test; (b) single-pump configuration for the smallest SWWM-1 module test (1.8"x12") and the intermediate SWWM-2 and SWWM-4 module tests (2.5"x40"); (c) two-pump configuration for the largest SWWM-3 module test (4.0"x40").

3.2.2.3 Analytical methods

Solute rejection (Rej_i) and permeate flux (J_{tol}) were calculated using Equations (2.1) and (2.2), respectively. The concentration of SoA was determined using a gas chromatograph with a flame ionisation detector and a fused silica column (Rtx® – 2887 column purchased from Thames Restek Limited, UK). The temperature programme ran from 40 to 300 °C at a rate of 15 °C min⁻¹, and then remained at 300 °C for 10 min. The flow rate of the carrier gas (helium) was set at 0.7 ml min⁻¹.

3.3 Modelling and analysis

3.3.1 Physical properties of solutions

In this chapter, the properties of SoA / EA solutions were determined using the Aspen Properties Estimate System. Dortmund modified UNIFAC (UNIF-DMD) method was applied as a base method. EA was selected from Aspen Properties database. As the UNIF-DMD parameters for SoA are not available in Aspen, the structure of SoA was defined by means of UNIF-DMD structural groups (see Table 3.2) and molecular weight (678.59 g mol⁻¹). The molecular structure of SoA is shown in Figure 3.3. NISTs Thermodynamic Engine was used to estimate all needed parameters for the two species.

Table 3.2: Structure of sucrose octaacetate by means of UNIF-DMD structural groups

Group code	Group	Number of appearance
1505	CH ₃ COO	8
1605	HC-O	3
1030	c-CH	5
1025	c-C	1
1010	CH ₂	3

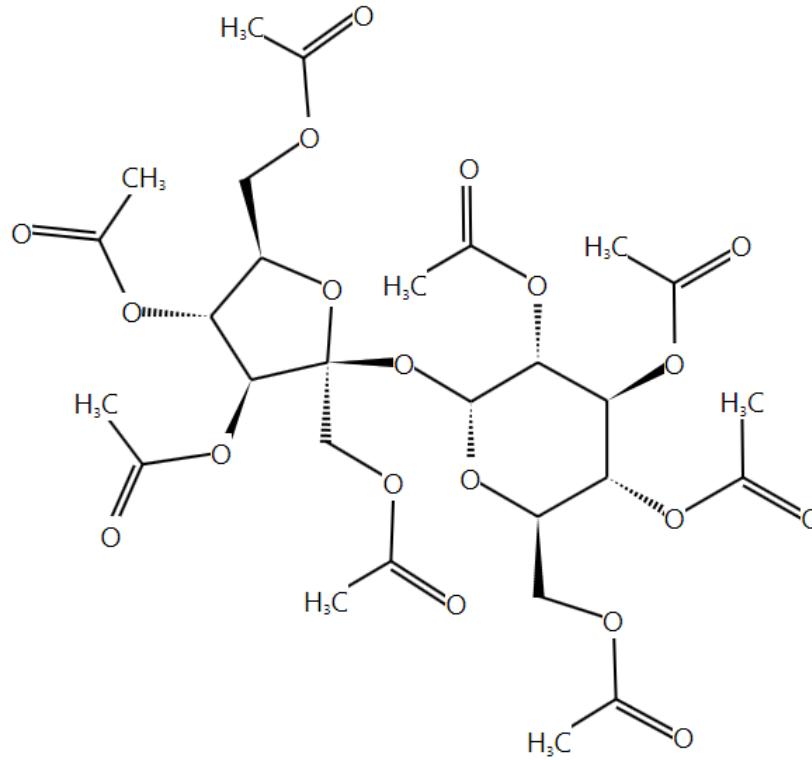


Figure 3.3: Molecular structure of sucrose octaacetate [109].

The calculated dynamic viscosity (η_f), density (ρ_f), activity coefficient of SoA (γ_{1f}), activity coefficient of EA (γ_{2f}) and diffusivity of SoA in EA (D_f), in the solutions with different concentrations of SoA at 30 °C, were correlated with second order polynomials. These correlations are shown as Equations (3.1) – (3.5).

$$\eta_f = (18.3w_{1f}^2 + 4.3w_{1f} + 4.1) \times 10^{-4} \quad \text{Equation (3.1)}$$

$$\rho_f = 330.1w_{1f}^2 + 70.1w_{1f} + 892.7 \quad \text{Equation (3.2)}$$

$$\gamma_{1f} = 12.1w_{1f}^2 - 8.91w_{1f} + 2.77 \quad \text{Equation (3.3)}$$

$$\gamma_{2f} = 0.213w_{1f}^2 + 0.0026w_{1f} + 1 \quad \text{Equation (3.4)}$$

$$D_f = (-6.59w_{1f}^2 - 28.6w_{1f} + 23.8) \times 10^{-10} \quad \text{Equation (3.5)}$$

w_{1f} is the mass fraction of SoA in the solution. The R^2 values of all these correlations are larger than 0.9995.

3.3.2 Procedure for regression and prediction

To study the fluid dynamics and mass transfer characteristics of the spiral-wound membrane modules, the following procedure, was performed:

- (a) a suitable membrane transport model was chosen to describe the transport through the membrane and experimental data for flat sheet membranes were used to perform regression and obtain the unknown model parameters;
- (b) experimental data for a 1.8"x12" spiral-wound membrane module were used to perform regression and obtain semi-empirical correlations for the pressure drop in both the feed and permeate channels and the mass transfer coefficient in the feed channel; The parameters describing the feed and permeate channels in the spiral-wound membrane module were also obtained in this regression step.
- (c) experimental data for larger spiral-wound membrane modules, fabricated using the same feed and permeate spacers, were used to validate the predictive capability of this procedure.

The procedure is schematically illustrated in Figure 3.4.

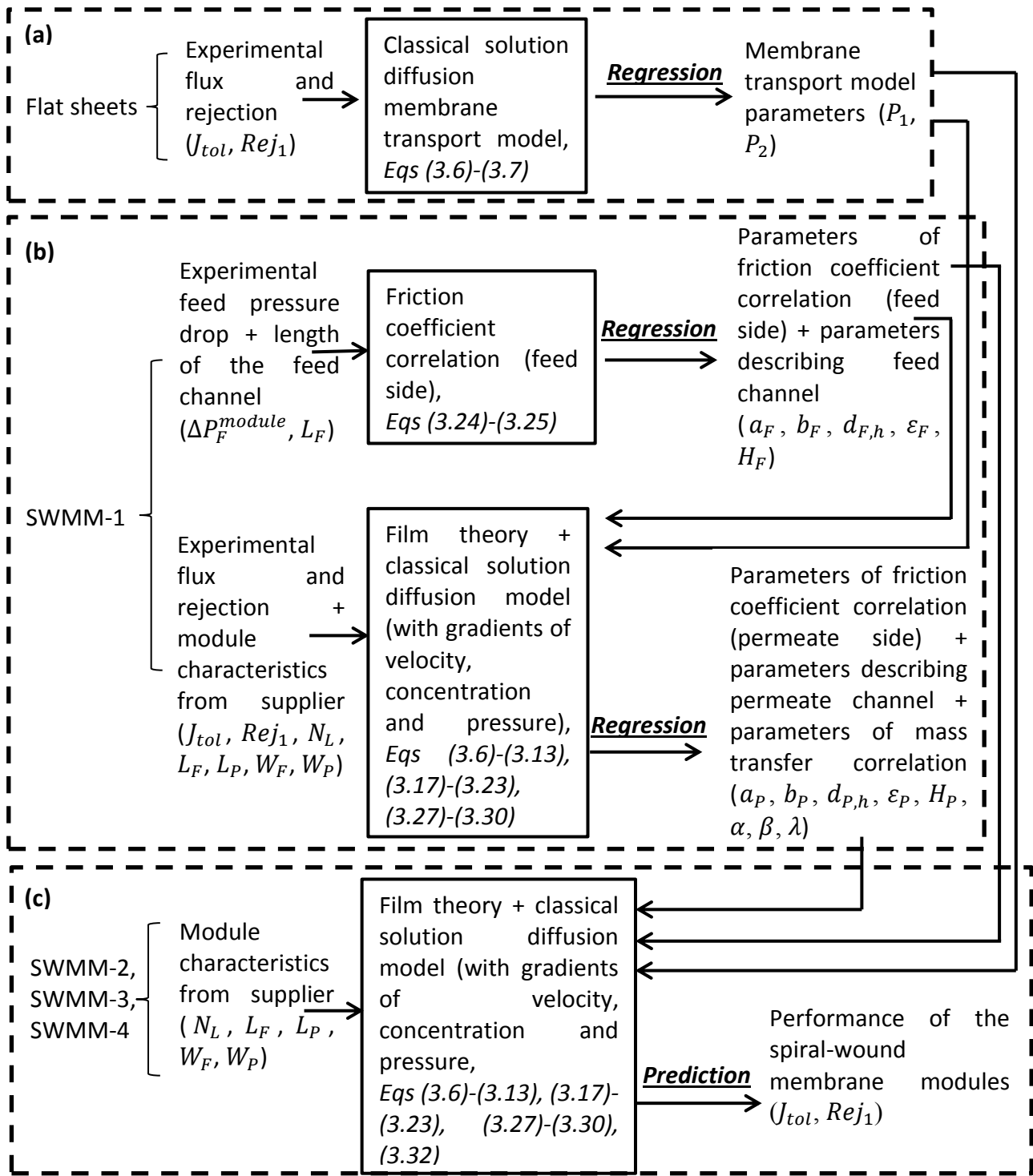


Figure 3.4: Schematic diagram of the procedure for regression and prediction used in this chapter. (a) Regression of the flat sheet experimental data to obtain the membrane transport model parameters; (b) regression of a 1.8"x12" module (SWMM-1) performance data to obtain semi-empirical expressions for the pressure drop in both the feed and permeate channels and the mass transfer coefficient in the feed channel, as well as the parameters describing the feed and permeate channels; (c) prediction of

performance for spiral-wound membrane modules of different sizes, but with the same feed and permeate spacers.

3.3.2.1 Membrane transport model and regression of the permeability coefficients

Both PuraMem® S600 and Lab-1 membranes used in this study are silicon coated rubber membranes, therefore according to Marchetti and Livingston [61], a classical SD model accounting for both concentration polarisation and thermodynamic non-ideality is used to describe the membrane transport. This model for a two-component system (one solute and one solvent) can be described as Equations (3.6) – (3.13).

$$J_1 = P_1[x_{1fm} - x_{1p} \frac{\gamma_{1p}}{\gamma_{1fm}} \exp(-\frac{v_1(P_f - P_p)}{RT})] \quad \text{Equation (3.6)}$$

$$J_2 = P_2[x_{2fm} - x_{2p} \frac{\gamma_{2p}}{\gamma_{2fm}} \exp(-\frac{v_2(P_f - P_p)}{RT})] \quad \text{Equation (3.7)}$$

$$J_{tol} = J_1 v_1 + J_2 v_2 \quad \text{Equation (3.8)}$$

$$\frac{C_{1fm} - C_{1p}}{C_{1f} - C_{1p}} = \exp(\frac{J_{tol}}{k_f}) \quad \text{Equation (3.9)}$$

$$x_{1fm} + x_{2fm} = 1 \quad \text{Equation (3.10)}$$

$$x_{1p} + x_{2p} = 1 \quad \text{Equation (3.11)}$$

$$x_{1fm} = \frac{C_{1fm}}{C_{1fm} + C_{2fm}} \quad \text{Equation (3.12)}$$

$$x_{1p} = \frac{C_{1p}}{C_{1p} + C_{2p}} \quad \text{Equation (3.13)}$$

P_i is the permeability coefficient for the species i ($i = 1$, solute; $i = 2$, solvent). k_f is the mass transfer coefficient in the feed side. J is the molar flux, x is the molar fraction, γ is the activity coefficient, v is the molar volume, P is the pressure, R is the ideal gas constant, T is the temperature, C is the concentration and J_{tot} is the total volumetric flux. The subscripts p , f and fm refer to the permeate side, the feed side and the feed side membrane-liquid interface, respective. The permeability coefficients of the classical SD model for SoA and EA (P_1 and P_2 , respectively) were determined by performing regression of the flat sheet flux and rejection data obtained at the lowest practical operating pressure of 5 bar with a retentate flowrate of 80 L h⁻¹ (see Figure (3.3(a))). To simplify the calculation, the following assumptions were made [39]: (i) negligible pressure drops through feed and permeate sides; (ii) negligible concentration polarisation; (iii) thermodynamically ideality of the system. The classical SD model was therefore simplified as:

$$J_1 = P_1[x_{1f} - x_{1p}\exp(-\frac{v_1 P_f}{RT})] \quad \text{Equation (3.14)}$$

$$J_2 = P_2[x_{2f} - x_{2p}\exp(-\frac{v_2 P_f}{RT})] \quad \text{Equation (3.15)}$$

The calculated permeability coefficients were used to predict the performance of the flat sheet membranes tested at different operating pressures, to further verify the suitability of this membrane transport model for the membranes used in this study. The capability of the model to perform regression was quantified in terms of norm of residuals, *resnorm*, as shown in Equation (3.16).

$$resnorm = \left(\frac{1}{Q-1} \sum_{q=1}^Q \left(\frac{z_{q,c} - \overline{z_{q,e}}}{\overline{z_{q,e}}} \right)^2 \right)^{0.5} \quad \text{Equation (3.16)}$$

In this equation, $z_{q,c}$, $\overline{z_{q,e}}$ and Q are the calculated data, average experimental data, and the number of the data, respectively.

3.3.2.2 Pressure drops and mass transfer characteristics in spiral-wound membrane modules

Permeate and feed channels in spiral-wound membrane modules were modelled as composed of $m \times n$ sufficiently small volumes in 2 dimensions, within which constant local pressure, concentration and velocity values were assumed. This is schematically shown in Figure 3.5.

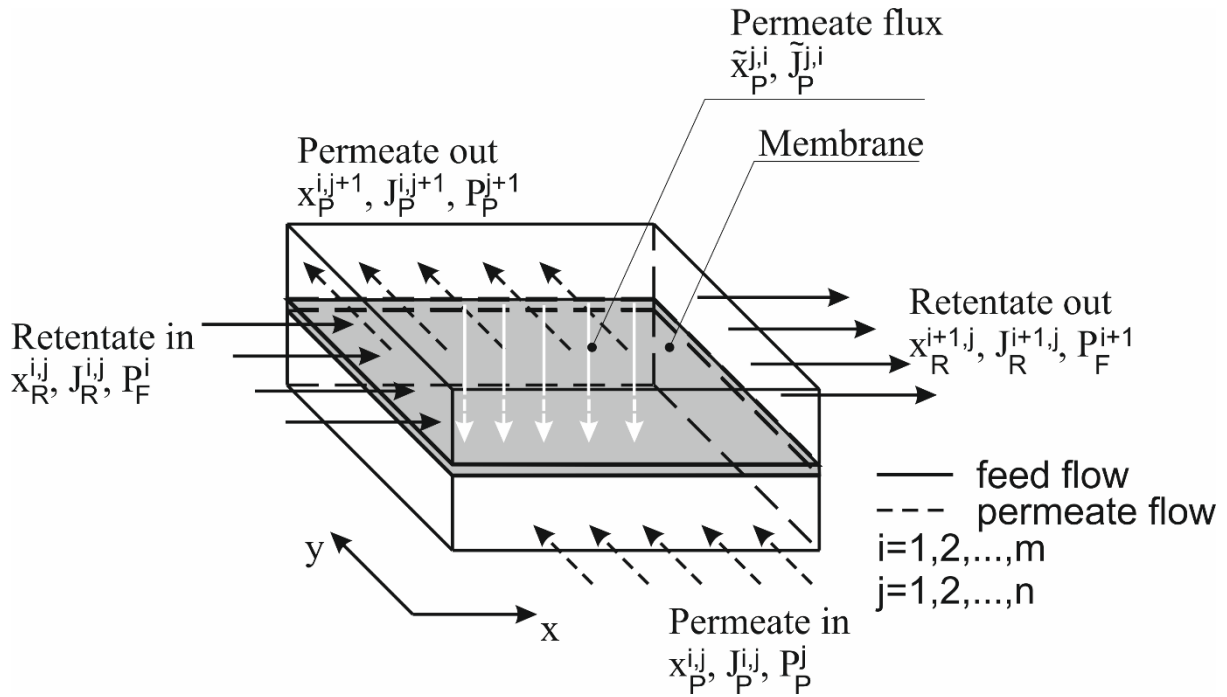


Figure 3.5: Schematic representation of an elemental volume of a spiral-wound membrane module, containing parts of the feed channel, the membrane layer and the permeate channel. Within each elemental volume, constant local pressure, concentration and velocity value were assumed.

The local permeate molar flowrate, $\tilde{J}_p^{i,j}$, and the local solute molar fraction, $\tilde{x}_p^{i,j}$, through each $i \times j$ membrane element was calculated as a function of the local feed and permeate pressures and concentrations, using the SD model, as described by Equations (3.6) – (3.7). As constant local pressures, velocity and concentrations were considered within each element, the flux and solute molar fraction through the element were calculated using the values of the parameters at the inlet of the element. One-dimensional convective flow was assumed along the x axis in the feed channel and along the y axis in the permeate channel. The concentration profiles along x and y directions were obtained as a result of consecutive solutions of the coupled membrane transport model (see Equations (3.6) - (3.13)) and the material balance equations (see Equations (3.17) - (3.20)) for each pair of $i \times j$ permeate and feed elemental volume.

$$J_p^{i,j+1} = J_p^{i,j} + \tilde{J}_p^{i,j} \quad \text{Equation (3.17)}$$

$$x_p^{i,j+1} J_p^{i,j+1} = x_p^{i,j} J_p^{i,j} + \tilde{x}_p^{i,j} \tilde{J}_p^{i,j} \quad \text{Equation (3.18)}$$

$$J_R^{i+1,j} = J_R^{i,j} - \tilde{J}_p^{i,j} \quad \text{Equation (3.19)}$$

$$x_R^{i+1,j} J_R^{i+1,j} = x_R^{i,j} J_R^{i,j} - \tilde{x}_p^{i,j} \tilde{J}_p^{i,j} \quad \text{Equation (3.20)}$$

J_R and J_p are the local molar flowrate of the retentate and permeate flow, respectively. $x_R^{i,j}$ is the local solute molar fraction in the retentate side and $x_p^{i,j}$ is the local solute molar fraction in the permeate side. The pressure drop through the feed channel was calculated using the friction coefficient correlation in the form of Equation (2.37). This equation was reformulated to describe the pressure drop along the elemental volume, as shown in Equation (3.21).

$$P_F^{i+1} = P_F^i - \frac{a_F}{2d_{F,h}} \left(\frac{\rho(\bar{x}_R^i) \bar{u}_{i,F} d_{F,h}}{\mu(\bar{x}_R^i)} \right)^{b_F} \rho(\bar{x}_R^i) \bar{u}_{i,F}^2 \Delta x^i \quad \text{Equation (3.21)}$$

a_F and b_F are the coefficient and the exponent of the Reynolds number in the friction coefficient correlation for the feed channel, respectively. $d_{F,h}$ is the hydraulic diameter of the feed channel and Δx^i is the length of the element $i \times j$ along x axis. In Equation (3.21), the average retentate mole fraction, $\bar{x}_R^i$, and the average linear fluid velocity, $\bar{u}_{i,F}$, for the entire cross section of the feed channel, at axial position x^i , were calculated according to Equations (3.22) and (3.23), respectively.

$$\bar{x}_R^i = \frac{\sum_{j=1}^n x_R^{i,j} J_R^{i,j}}{\sum_{j=1}^n J_R^{i,j}} \quad \text{Equation (3.22)}$$

$$\bar{u}_{i,F} = \frac{\sum_{j=1}^n J_R^{i,j} v(\bar{x}_R^i)}{N_L \times H_F L_F \varepsilon_F} \quad \text{Equation (3.23)}$$

ε_F is the void fraction of the feed spacer, H_F is the height of the feed spacer, N_L is the number of the membrane leaves, L_F is the length of the feed channel. The unknown parameters describing the coefficient and the exponent of the Reynolds number in the friction coefficient correlation for the feed channel (a_F and b_F) and the geometry of the feed channel ($d_{F,h}$, ε_F and H_F) were obtained from regression of the pressure drop data through the feed channel of the 1.8"x12" SWMM-1 module. In the SWMM-1 module, the maximum cut-off (the ratio of the permeate flow rate to the feed flow rate) was lower than 3 %. It was therefore assumed that the concentration and velocity in the feed channel were uniform. The final correlation for the overall feed pressure drop in the module therefore, can be described by Equations (3.24) and (3.25).

$$\Delta P_F^{module} = \frac{a_F}{2d_{F,h}} \left(\frac{\rho(x_F^{inlet}) u_F^{inlet} d_{F,h}}{\mu(x_F^{inlet})} \right)^{b_F} \rho(u_F^{inlet})^2 L_F \quad \text{Equation (3.24)}$$

$$u_F^{inlet} = \frac{J_F^{inlet} v(x_F^{inlet})}{(N_L \times H_F L_F \varepsilon_F)} \quad \text{Equation (3.25)}$$

x_F^{inlet} , u_F^{inlet} and J_F^{inlet} are the solute molar fraction, the velocity and the molar flow rate in the feed inlet, respectively. The pressure drop of the module, ΔP_F^{module} , was measured experimentally, as the difference between the pressure drop in the housing in the presence of the module, $\Delta P_F^{module+housing}$, and the pressure drop of the empty housing $\Delta P_F^{empty housing}$ (see Equation (3.26)).

$$\Delta P_F^{module} = \Delta P_F^{module+housing} - \Delta P_F^{empty housing} \quad \text{Equation (3.26)}$$

The unknown parameters (a_F , b_F , $d_{F,h}$, ε_F and H_F) were obtained from regression of the 12 experimental pressure drop data through the feed channel of the 1.8"x12" SWMM-1 module (ΔP_F^{module}) using Equations (3.24) and (3.25) (see Figure 3.3(b)).

The pressure drop through the permeate channel was also calculated using the friction coefficient correlation in the form of Equation (2.37), and this equation was reformulated as Equation (3.27), to describe the permeate pressure drop along the elemental volume.

$$P_P^{j+1} = P_P^j - \frac{a_P}{2d_{P,h}} \left(\frac{\rho(x_P^{i,j}) u_{i,j,P} d_{P,h}}{\mu(x_P^{i,j})} \right)^{b_P} \rho u_{i,j,P}^2 \Delta y^j \quad \text{Equation (3.27)}$$

a_P and b_P are the coefficient and the exponent of the correlation for the friction coefficient in the permeate channel, represented by Equation (3.37), respectively. $d_{P,h}$ is the hydraulic diameter in the permeate channel and Δy^j is the length of the element $i \times j$ along y axis. The pressure in the outlet of the permeate channel (close to the central permeate tube) was assumed to be the atmospheric pressure. The local velocity in the permeate channel ($u_{i,j,P}$) was calculated as Equation (3.28).

$$u_{i,j,P} = \frac{2 \times J_P^{i,j} v(x_P^{i,j})}{\Delta x^i H_P \varepsilon_P} \quad \text{Equation (3.28)}$$

H_P is the height of the permeate channel and ε_P is the void fraction of the permeate channel. On the permeate side of the module, it is not possible to experimentally measure the pressure drop through the permeate channel, since three sides of the permeate channel are sealed by glue lines. Thus it is not possible to apply direct regression to obtain the parameters describing the coefficient and the exponent of the Reynolds number in the friction coefficient correlation for the permeate channel (a_P and b_P), and the geometry of the permeate channel ($d_{P,h}$, ε_P and H_P). Similarly, the coefficient and the exponents in the Sherwood number correlation for the feed channel (α , β and λ), represented by Equations (3.29) and (3.30), cannot be obtained by performing direct regression of the mass transfer coefficient data, since the mass transfer coefficient was not experimentally measured. Here the convective mass transfer on the film attributed by the permeate flux is ignored, in agreement with Schock and Miquel [88], since the permeation velocities are orders of magnitude smaller compared to the convective cross-flow velocities in the feed channels.

$$Sh = \frac{k_F^{i,j} d_{F,h}}{D_{(x_R^{i,j})}} = \alpha Re^\beta Sc^\lambda = \alpha \left(\frac{d_{F,h} \rho_{(x_R^{i,j})} u_{i,j,F}}{\mu_{(x_R^{i,j})}} \right)^\beta \left(\frac{\mu_{(x_R^{i,j})}}{\rho_{(x_R^{i,j})} D_{(x_R^{i,j})}} \right)^\lambda \quad \text{Equation (3.29)}$$

$$u_{i,j,F} = \frac{\sum_{j=1}^n J_R^{i,j} v(x_R^{i,j})}{N_L \times H_F L_F \varepsilon_F} \quad \text{Equation (3.30)}$$

$u_{i,j,F}$ is the local velocity in the feed channel. All 8 unknown parameters (a_P , b_P , $d_{P,h}$, ε_P , H_P , α , β and λ) were therefore determined together by performing indirect regression of the experimental flux and rejection data through the SWMM-1 module (in total, 36 flux data and 27 rejection data were available) using the combination of the film theory and the classical solution diffusion model, considering the gradients of concentrations, pressures and velocities (see Figure 3.3(b)). The pre-determined classical

solution-diffusion permeability coefficients, the friction coefficient correlation in the feed channel and the parameters describing the geometry of the feed channel were used in this step.

All regressions were performed in the MATLAB environment, using the built-in function *lsqcurvefit*. The regression implements a local search mechanism (i.e. gradient search) to obtain solutions that optimise the associated criterion function. The function uses a “trust-region-reflective” algorithm, which requires a determined or overdetermined system of equations. It means that the number of independent equations must be at least equal to the number of fitting parameters. In this work, an overdetermined system was applied to perform all regressions, to minimise the effect of possible experimental outliers.

3.3.2.3 Prediction of performance for spiral-wound membrane modules of different size and / or fabricating using different types of membranes

The SWMM-2 and SWMM-3 modules were fabricated with the same type of feed and permeate spacers and with the same membranes as the SWMM-1 module, but with larger sizes (2.5"x40" and 4.0"x40", respectively). In the 4.0"x40" SWMM-3 module test, the solute concentration of the feed solution at the inlet of the module (C_{1f}) was different from the concentration of the starting solution in the feed tank (C_{1ft}), due to the two-pump configuration system (see Figure 3.2(c)). The concentration of the feed solution at the inlet of the module (C_{1f}) was calculated according to a mass balance on both inner and outer loops (see Equation (3.31)).

$$C_{1f} = \frac{(F_r' + F_p)C_{1ft}}{F_r + F_p} + \frac{(F_r - F_r')(F_p + F_r')C_{1ft} - F_p C_{1p}}{F_r'} \quad \text{Equation (3.31)}$$

F_r and F_r' are the retentate flowrates after the module and the back pressure valve, respectively (see Figure 3.2(c)). F_p is the permeate flowrate. Since the system under study is a highly rejected system ($C_p \approx 0$), Equation (3.31) was simplified as Equation (3.32):

$$C_{1f} = \frac{(F_r' + F_p)C_{1ft}}{F_r + F_p} + \frac{(F_r - F_r')(F_p + F_r')C_{1ft}}{F_r + F_p} \frac{F_r'}{F_r'} \quad \text{Equation (3.32)}$$

It is assumed that the geometry of the channels is the same for modules made of the same spacers but different sizes and/or membranes. The performance of the SWMM-2 and SWMM-3 modules was then predicted using the combination of the film theory and the classical SD model, considering the gradients of pressures, concentrations and velocities, based on the pre-determined membrane transport model parameters; the semi-empirical correlations for the friction coefficient in both the feed and permeate channels; the semi-empirical correlation for the mass transfer coefficient in the feed channel and the pre-determined parameters describing the geometry of the feed and permeate channels (see Figure 3.3(c)).

On the other hand, the 2.5"x40" SWMM-4 module was fabricated with a different type of membrane (Lab-1) but with the same feed and permeate spacers as the other 3 modules. The membrane permeability coefficients for the Lab-1 membrane were again obtained by performing regression of experimental data for the flat sheet Lab-1 membrane (flux and rejection) using Equations (3.14) and (3.15). Afterwards, the same prediction procedure as for the SWMM-2 and SWMM-3 modules was performed (see Figure 3.3(c)).

3.4 Results and discussion

3.4.1 Effects of time and pressure on membrane performance

OSN polymeric membranes can compact over time and under pressure, as a consequence of their more or less open structure and crosslinking degree [61]. In order to understand the transport through the membranes in this study, it is important to check whether any irreversible compaction occurs under pressure and over time. Figure 3.6 shows the performance of both PM S600 and Lab-1 flat sheet membranes, tested in 1 g L⁻¹ SoA in EA solution, over time and at different pressure values. In Figure 3.6, the bars represent the deviation of the experimental data among the 8 cells. The permeance through both

membranes is almost independent of the pressure (see Figure 3.6(a)), while the rejection is positively affected by the pressure: the higher the pressure, the higher the rejection (see Figure 3.6(b)). Moreover, the membrane performance (in terms of both flux and rejection) of both membranes showed negligible change after the membranes were compressed at high pressure, indicating that these membranes do not undergo any significant irreversible compaction.

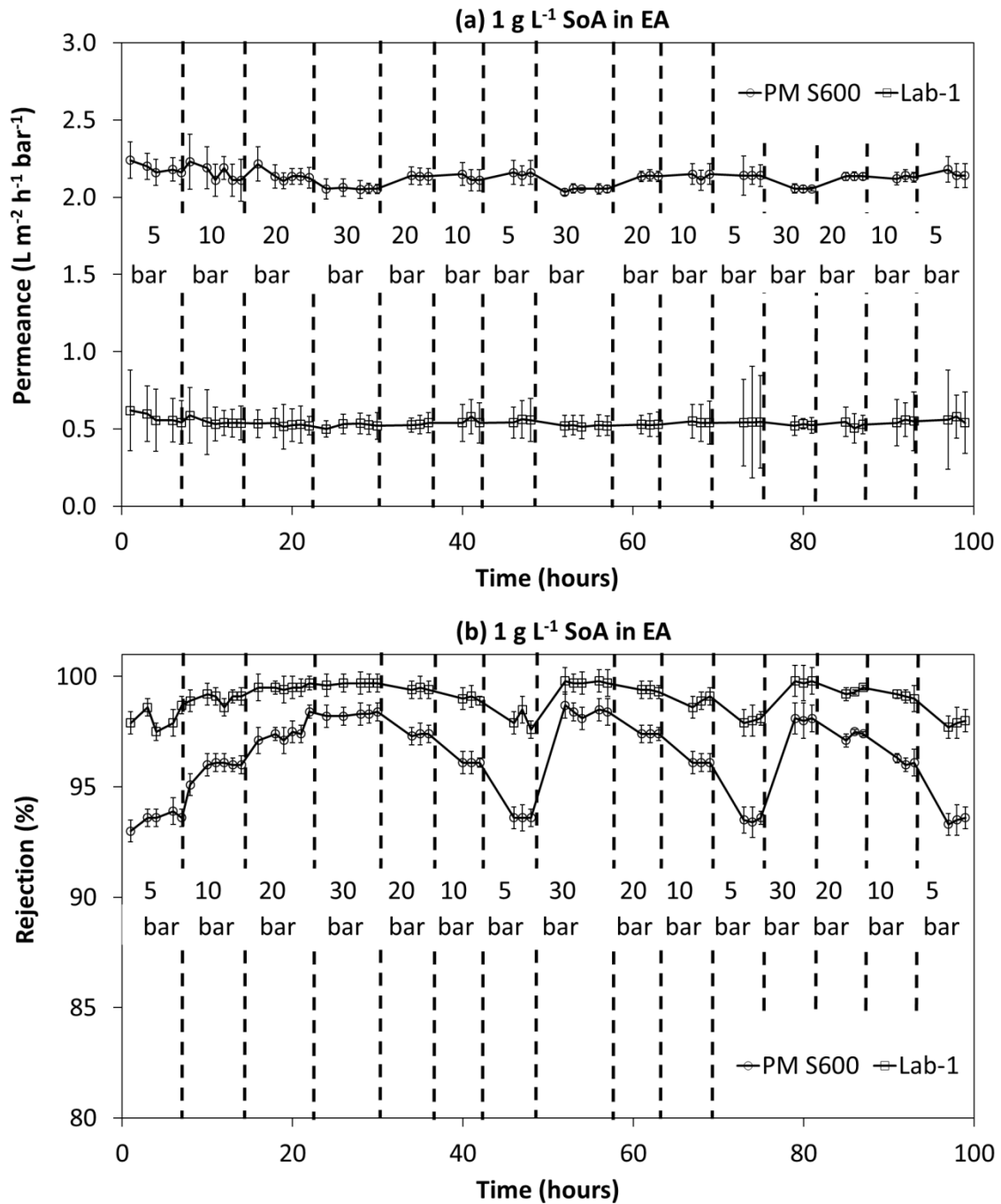


Figure 3.6: Performance of flat sheet PuraMem® S600 and Lab-1 membranes tested in 1 g L⁻¹ SoA in EA solution at 30 °C and various pressures over time. (a) Permeance; (b) rejection of SoA.

3.4.2 Regression of flat sheet membrane data to obtain the permeability coefficients

The membrane transport model parameters for both PM S600 and Lab-1 membranes were determined by regressing the performance of flat sheet data at 5 bar, using the SD model, represented by Equations (3.14) and (3.15). The model parameters to be determined are the solute and solvent permeability coefficients, respectively. The regressed values of these parameters are reported in Table 3.3.

Table 3.3: Membrane transport model parameters for PuraMem® S600 and Lab-1 membranes: P_1 is the solute permeability coefficient and P_2 is the solvent permeability coefficient

	PuraMem® S600	Lab-1
P_1 (mol m ⁻² s ⁻¹)	2.06E-3	1.66E-4
P_2 (mol m ⁻² s ⁻¹)	1.59	0.40

These transport parameters were then used to predict the performance of the same flat sheet membranes at different pressure values, from 5 to 30 bar. Good agreement between calculated and experimental flux and rejection was observed, as shown in Figure 3.7(a) and (b), respectively. In Figure 3.7, the bars represented the deviation of the experimental data among the 8 cells. The values of *resnorm* for PM S600 and Lab-1 membranes are 9.1E-03 and 4.2E-02, respectively. These very small values confirmed that the classical SD model is suitable to describe the membrane transport through these two types of membranes at different pressures, in alignment with Marchetti and Livingston [61].

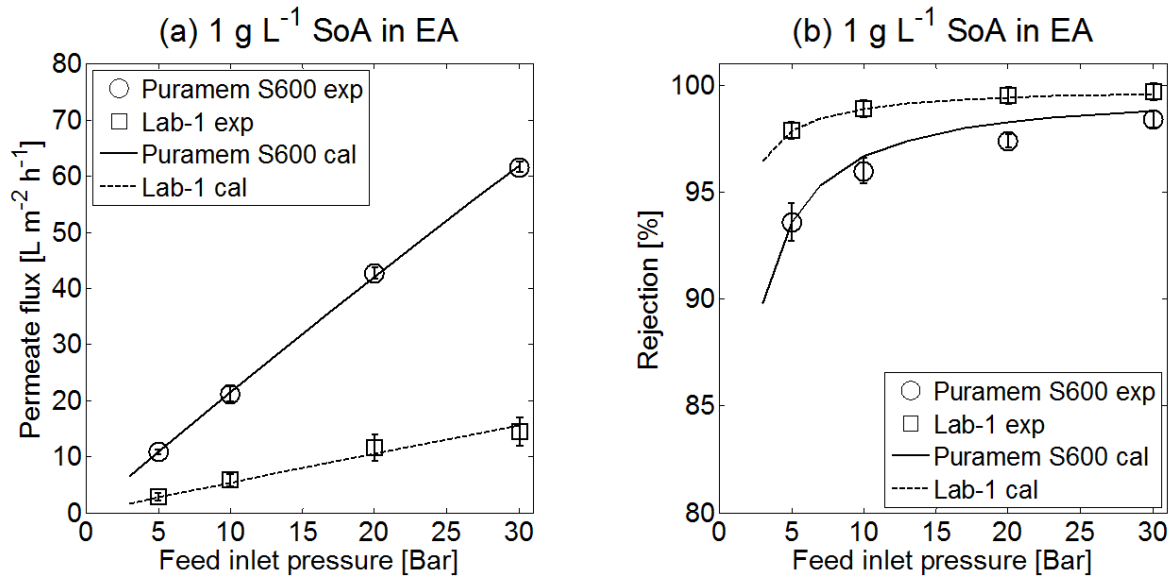


Figure 3.7: Experimental and calculated performance of flat sheet PuraMem® S600 and Lab-1 membranes tested in 1 g L⁻¹ SoA in EA solution at 30 °C and various pressures. (a) Permeate flux; (b) rejection of SoA.

3.4.3 Regression of SWMM-1 module performance to obtain the correlations for pressure drop and mass transfer coefficient in the feed channel and the spacer geometry

The coefficient and the exponents in the friction coefficient correlation for the feed channel (a_F and b_F) and the parameters describing the feed channel geometry ($d_{F,h}$, ε_F and H_F) were determined by regressing the feed pressure drop data in the SWMM-1 module, using Equations (3.24) and (3.25). The correlation for the friction coefficient in the feed channel thus obtained is represented as Equation (3.33).

$$f_F = a_F Re^{b_F} = a_F \left(\frac{d_{F,h} \rho_F u_F}{\mu_F} \right)^{b_F} \quad \text{Equation (3.33)}$$

$$= 6.94 Re^{-0.34}$$

The values of the parameters describing the hydraulic diameter ($d_{F,h}$), void fraction (ε_F) and height of the feed channel (H_F) are 0.79 mm, 0.827 and 0.77 mm, respectively. Good agreement between the calculated and the experimental pressure drop data for the SWMM-1 module, characterised by a *resnorm* of 3.1E-02, is shown in Figure 3.8(a). Furthermore, good prediction of the feed pressure drop in the other three

modules is also shown in Figures 3.8(b), (c) and (d). The *resnorm* values in the SWMM-2, SWMM-3 and SWMM-4 modules were 1.0E-02, 8.7E-02 and 5.6E-02, respectively. This proves that the friction coefficient correlation for the feed channel and the parameters describing the geometry of the feed channel, obtained from the regression of the SWMM-1 module performance data, successfully describe the pressure drop in the channels filled with the same feed spacer.

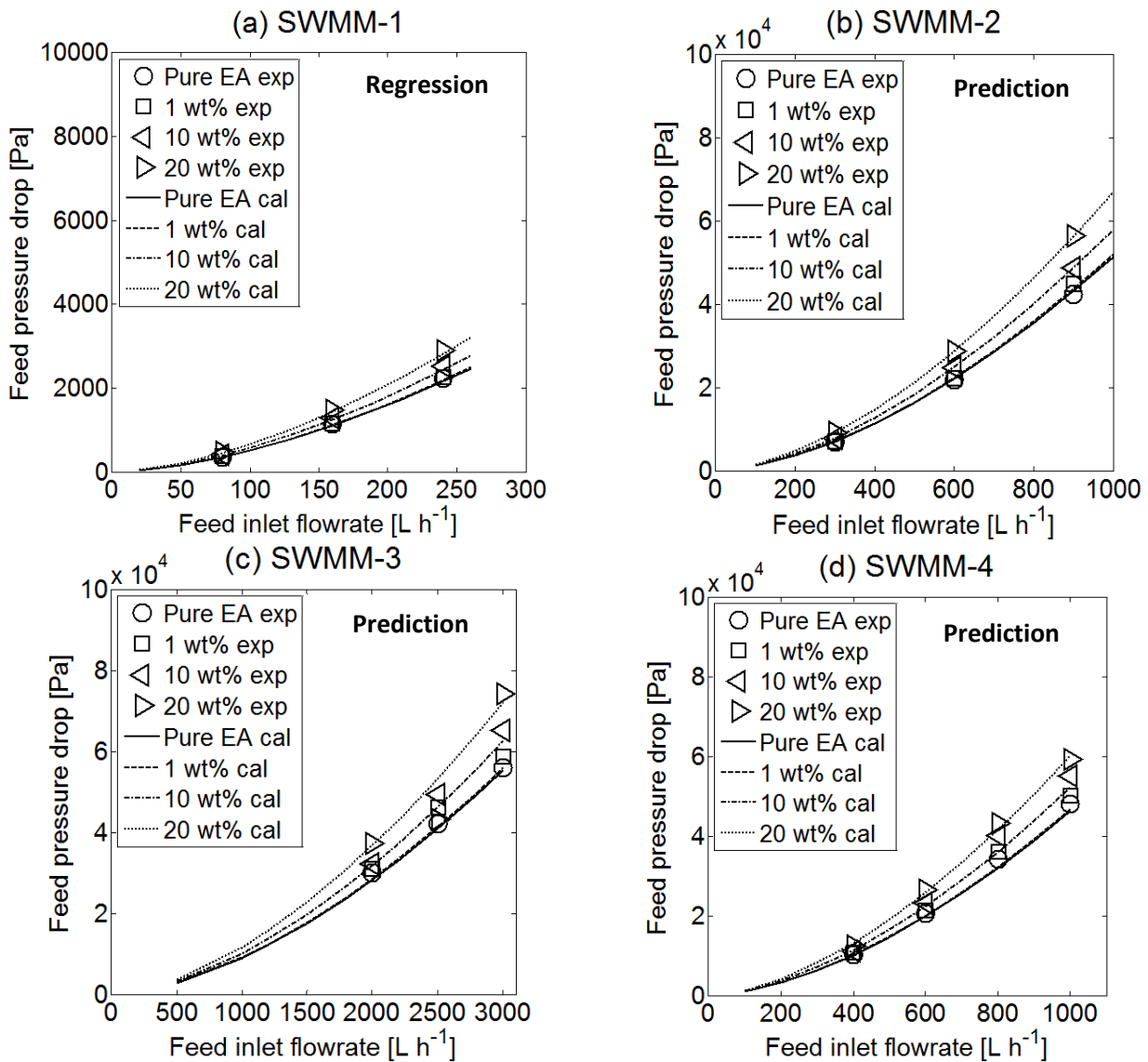


Figure 3.8: Experimental and calculated pressure drop through the feed channel of different modules: (a) 1.8"x12" SWMM-1; (b) 2.5"x40" SWMM-2; (c) 4.0"x40" SWMM-3; (d) 2.5"x40" SWMM-4. Data from (a) only were used in the regression procedure.

It is worth noting that the feed pressure drop through all the modules is low (< 1 bar). Although the feed pressure drop is negligible for the simulation, it is decided to include it in the modelling procedure anyway, to keep the modelling framework as generic as possible. In fact, feed pressure drops may be more significant in other industrial configurations, such as arrays of several SWMMs connected in series [27, 10].

The coefficient and the exponent of the Reynolds number in the friction coefficient correlation for the permeate channel (a_p and b_p), the parameters describing the permeate channel ($d_{p,h}$, ε_p and H_p) and the coefficient and the exponents in the Sherwood number correlation (α , β and λ) were determined by performing regression of the SWMM-1 module performance (flux and rejection), using the combination of the film theory and the classical SD model, considering gradients of pressures, concentrations and velocities. The regression made use of the permeability coefficients, the friction coefficient correlation for the feed channel and the parameters describing the feed channel obtained from previous regression procedures. It is important to note that, in this step, both fluid dynamics and mass transfer characteristics were regressed at the same time. The friction coefficient correlation for the permeate channel is described by Equation (3.34) and the Sherwood number correlation for the feed channel is described by Equation (3.35), respectively.

$$f_p = a_p Re^{b_p} = a_p \left(\frac{d_{p,h} \rho_p u_p}{\mu_p} \right)^{b_p} \quad \text{Equation (3.34)}$$

$$= 16 Re^{-0.34}$$

$$Sh = \alpha Re^\beta Sc^\lambda \quad \text{Equation (3.35)}$$

$$= 0.075 Re^{0.61} Sc^{0.33}$$

The values of the hydraulic diameter ($d_{p,h}$), void fraction (ε_p) and height of the permeate channel (H_p) are 0.048 mm, 0.315 and 0.27 mm, respectively. Good agreement between experimental and calculated

membrane module performance, characterised by a *resnorm* value of 6.1E-02, is shown in Figure 3.9, in terms of both membrane flux and rejection.

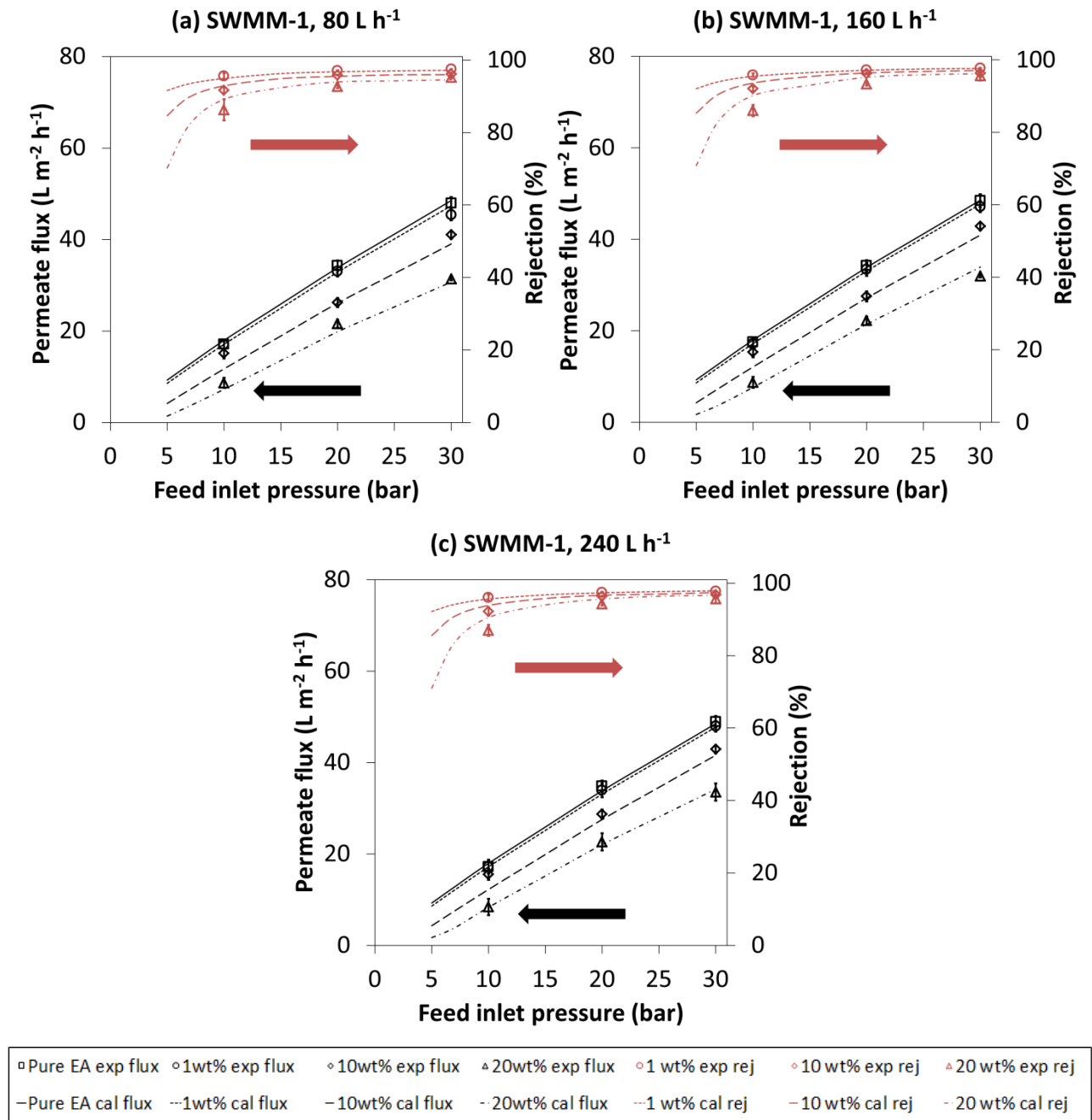


Figure 3.9: Experimental and calculated flux (black) and rejection (red) of the 1.8"x12" SWMM-1 module tested in 0 – 20 wt% SoA in EA solutions at 30 °C and various pressures (10, 20 and 30 bar) with different retentate flowrates: (a) 80 L h⁻¹; (b) 160 L h⁻¹; (c) 240 L h⁻¹. The performance of the 1.8"x12" SWMM-1

module was used for regression to obtain the correlations for characterising pressure drops and mass transfer as well as the parameters describing both feed and permeate spacers.

When comparing the permeance of the SWMM-1 module fabricated with the PM S600 membrane with the flat sheet PM S600 membrane in pure EA, it is noticeable that the permeate flux through the SWMM-1 module is lower (see Figure 3.10(a)): specifically, the higher the feed pressure, the bigger the difference between module flux and flat sheet membrane flux. The main reason for this divergence is the presence of the pressure drop in the permeate channel, which causes a reduction in the effective differential pressure between the retentate and permeate channels in the module with increasing feed pressure. The extent of the pressure drops in both the feed and permeate channels in the SWMM-1 module, at different operating pressures (10 – 30 bar), is shown in Figures 3.10(b), (c) and (d). Clearly, at 30 bar, the pressure drop is more significant than at 10 bar (see Figures 3.10(d) and (b)).

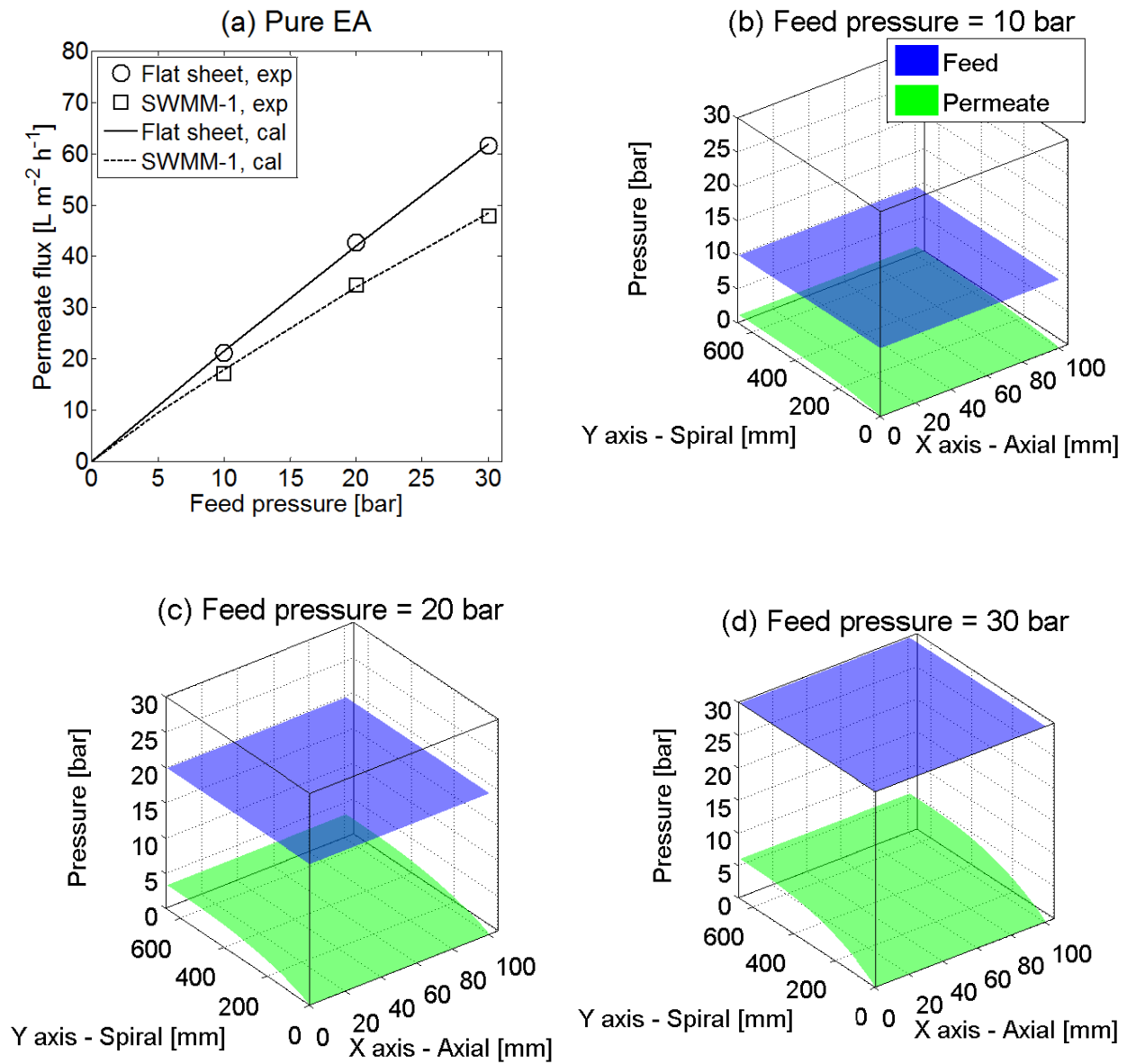


Figure 3.10: Permeate flux and pressure profiles through the SWMM-1 module tested in pure EA at 30 °C and different pressures, with a retentate flowrate of 80 L h⁻¹. (a) Experimental and calculated permeate flux through flat sheet PM S600 membranes and the SMWW-1 module; (b) pressure profile in both feed and permeate channels in the SWMM-1 module at the initial feed pressure of 10 bar; (c) pressure profile in both feed and permeate channels in the SWMM-1 module at the initial feed pressure of 20 bar; (d) pressure profile in both feed and permeate channels in the SWMM-1 module at the initial feed pressure of 30 bar.

As shown in Figure 3.11, the mass transfer coefficient in the SWMM-1 module had an order of magnitude of 10^{-5} m s^{-1} . Although gradients of velocity and concentration were present along the module, the mass transfer coefficient was found to be almost constant along the feed channel.

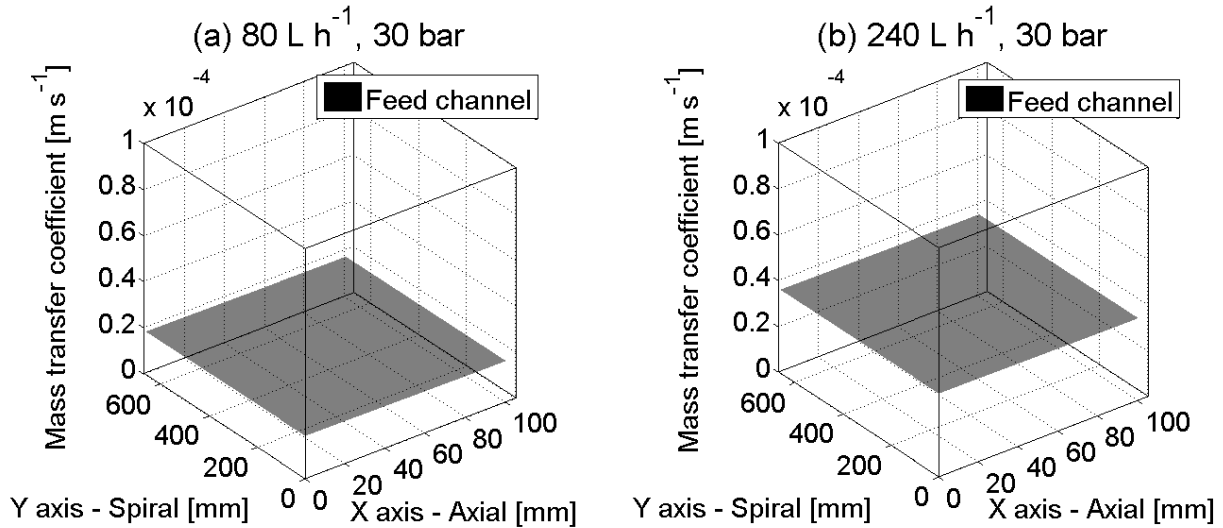


Figure 3.11: Profiles of mass transfer coefficient in the feed channel of the SWMM-1 module in 1 wt% SoA in EA solution at 30 bar with different retentate flowrates: (a) 80 L h^{-1} ; (b) 240 L h^{-1} .

Finally, the correlations found in this work, for both friction coefficient and mass transfer coefficient, were compared with similar correlations from the literature [88, 93, 100]. These correlations were used to predict flux and SoA rejection in the SWMM-1 module. Figure 3.12 clearly shows that the correlations from references [88, 93, 100], mainly obtained from indirect measurements and CFD simulations in aqueous solutions, were not suitable to describe the performance of the SWMM-1 module, while the correlations developed in this chapter provided the best match with the experimental data. The biggest improvement of the correlations developed in this chapter, with respect to those from literature, was found in the description of the solvent flux in pure EA (see Figure 12(a)) and in the description of the total volumetric flux and the solute molar flux under high pressure conditions in highly concentrated solution (see Figures 3.12(b) and (c)). One possible reason for the difference is that the valid range of the Reynolds and Schmidt

numbers in the correlations adopted from the literature is not exact the same as the range in this work. Specifically, in Figure 3.12(a), the Reynolds number in the feed channel was about 45 and it was between 5 and 19 in the permeate channel. The correlations adopted from Schock and Miquel [88] for the friction coefficients in both feed and permeate channels were validated in the Reynolds number range of 50 – 1,000 and 20 – 100, respectively. In Figures 12(b) and (c), the Reynolds and Schmidt numbers in the feed channel were about 250 and 440, respectively, and the correlations adopted from the literature were validated in different ranges: [88] for $150 < Re < 400$, $Sc = 660$; [93] for $90 < Re < 700$, $Sc = 2.09E5$; [100] for $50 < Re < 200$, $1,450 < Sc < 5,550$. It is also worth mentioning that the range of Reynolds and Schmidt numbers in OSN is wide due to the variety of solutes and solvents, and very likely the correlations derived from aqueous solutions cannot cover the ranges of Reynolds and Schmidt numbers for OSN applications.

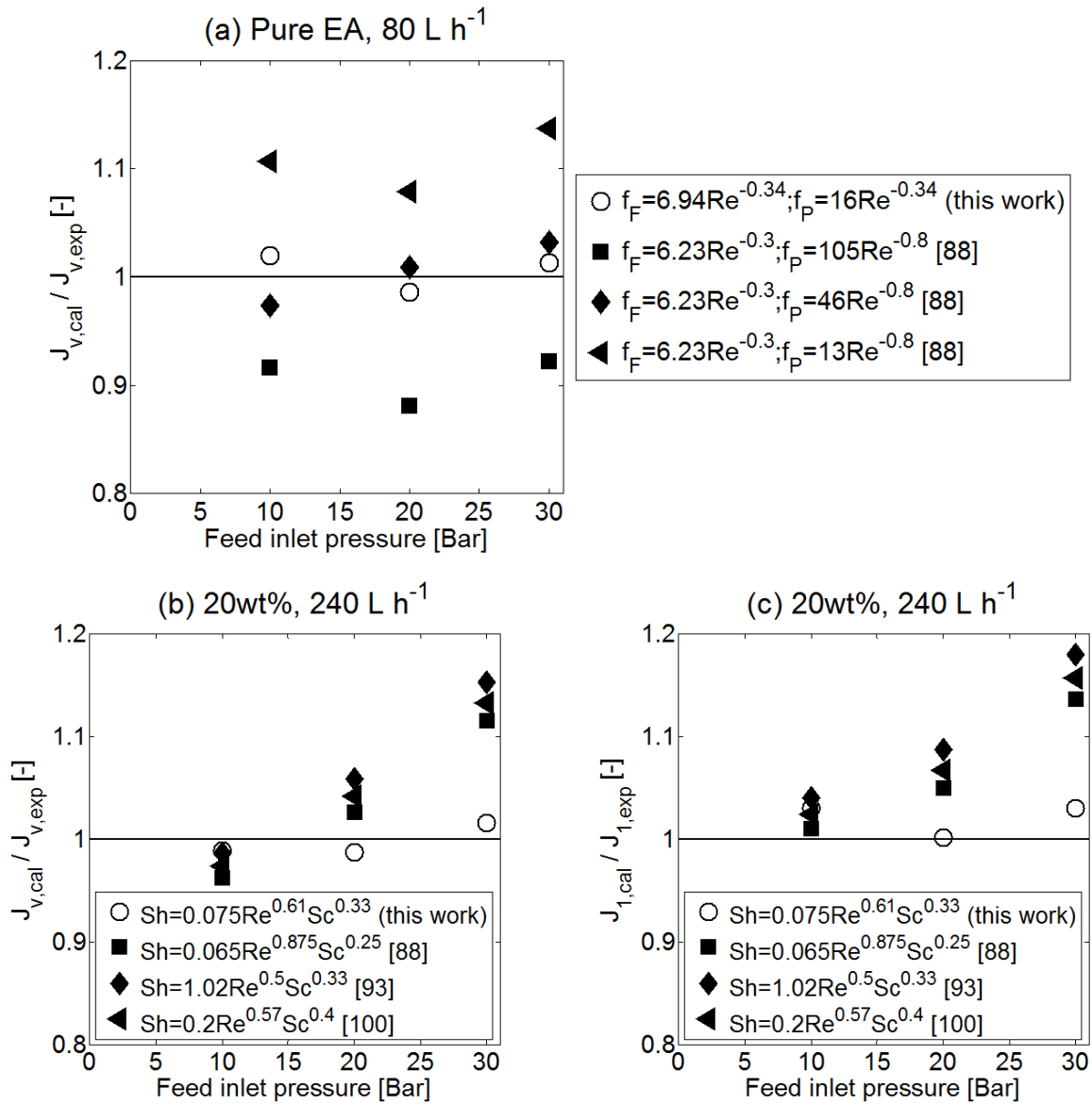


Figure 3.12: Calculated total volumetric flux and SoA molar flux in the SWMM-1 module, normalised with respect to the experimental data. (a) Calculated total volumetric flux in the SWMM-1 module in pure EA at 30 °C and various pressures with a retentate flowrate of 80 L h⁻¹ using different friction coefficient correlations from this chapter and from Schock and Miquel [88]; (b, c) Calculated total volumetric flux (b) and SoA molar flux (c) in the SWMM-1 module in 20 wt% solution at 30 °C and various pressures with a retentate flowrate of 240 L h⁻¹ using the friction coefficient correlations from this chapter and different mass transfer correlations from this chapter and from Schock and Miquel [88], Schwinge et al. [93], Koutsou et al. [100].

3.4.4 Prediction of spiral-wound membrane module performance

Figures 3.13 – 3.15 show both experimental and predicted fluxes and rejections in all the modules not used in the regression procedure, under various operating conditions. It is clear that both fluxes and rejections decreased when the concentration of the solution increased, due to the osmotic pressure and concentration polarisation. Furthermore, the figures show that both the fluxes and rejections increased with increasing the feed pressure. More importantly, good agreement between the experimental and predicted data, characterised by the small values of *resnorm* (6.9E-02, 6.1E-02 and 9.1E-02 for the SWMM-2, SWMM-3 and SWMM-4 modules, respectively), was observed in all cases.

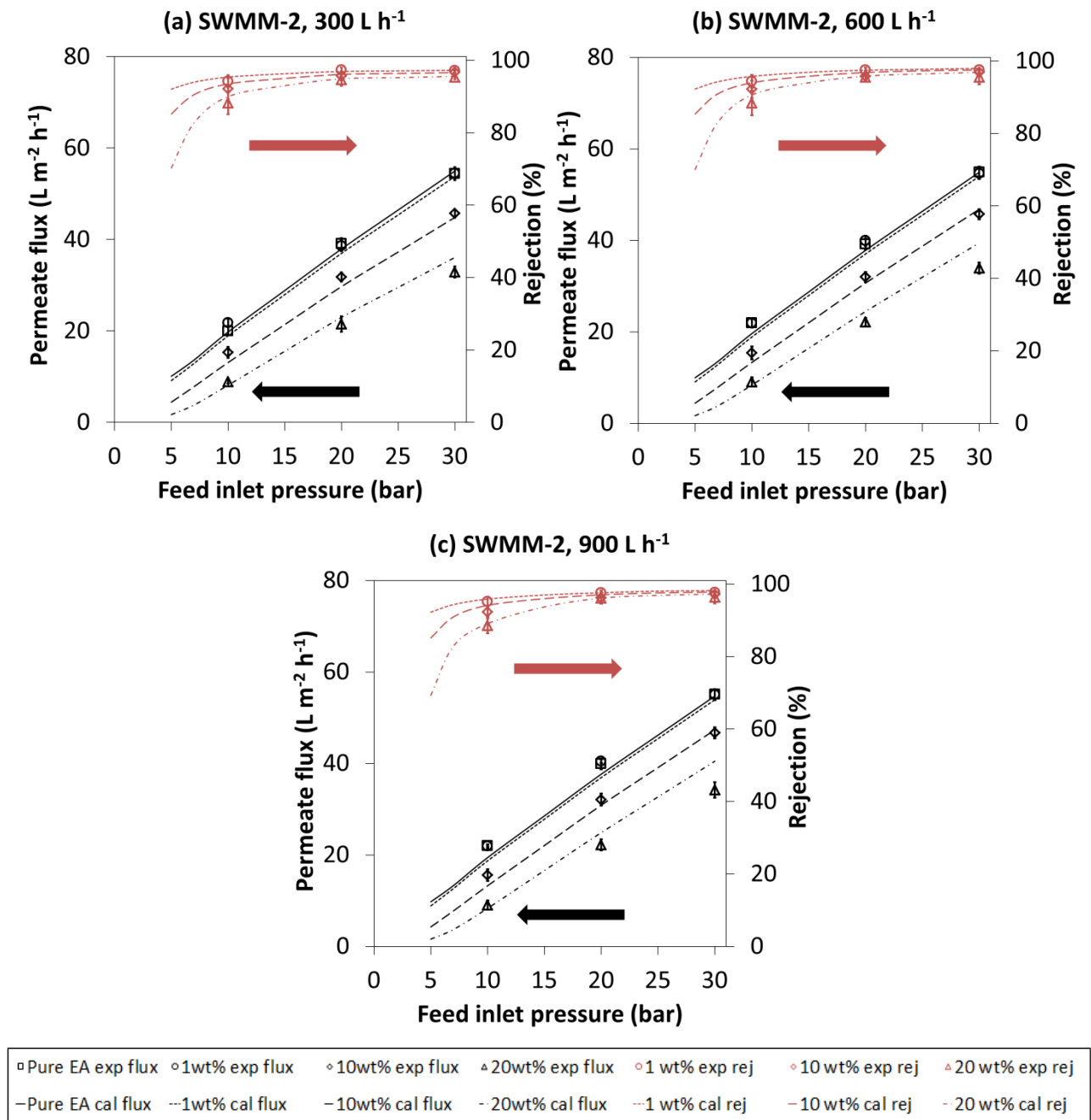


Figure 3.13: Experimental and calculated flux (black) and rejection (red) of the 2.5"x40" SWMM-2 module tested in 0 – 20 wt% SoA in EA solutions at 30 °C and various pressures (10, 20 and 30 bar) with different retentate flowrates: (a) 300 L h⁻¹; (b) 600 L h⁻¹; (c) 900 L h⁻¹. The performance of the 2.5"x40" SWMM-2 module was not used in the regression procedure. Rather, the regressed parameters were used to simulate the performance of this module and validate the model by comparing to experimental data.

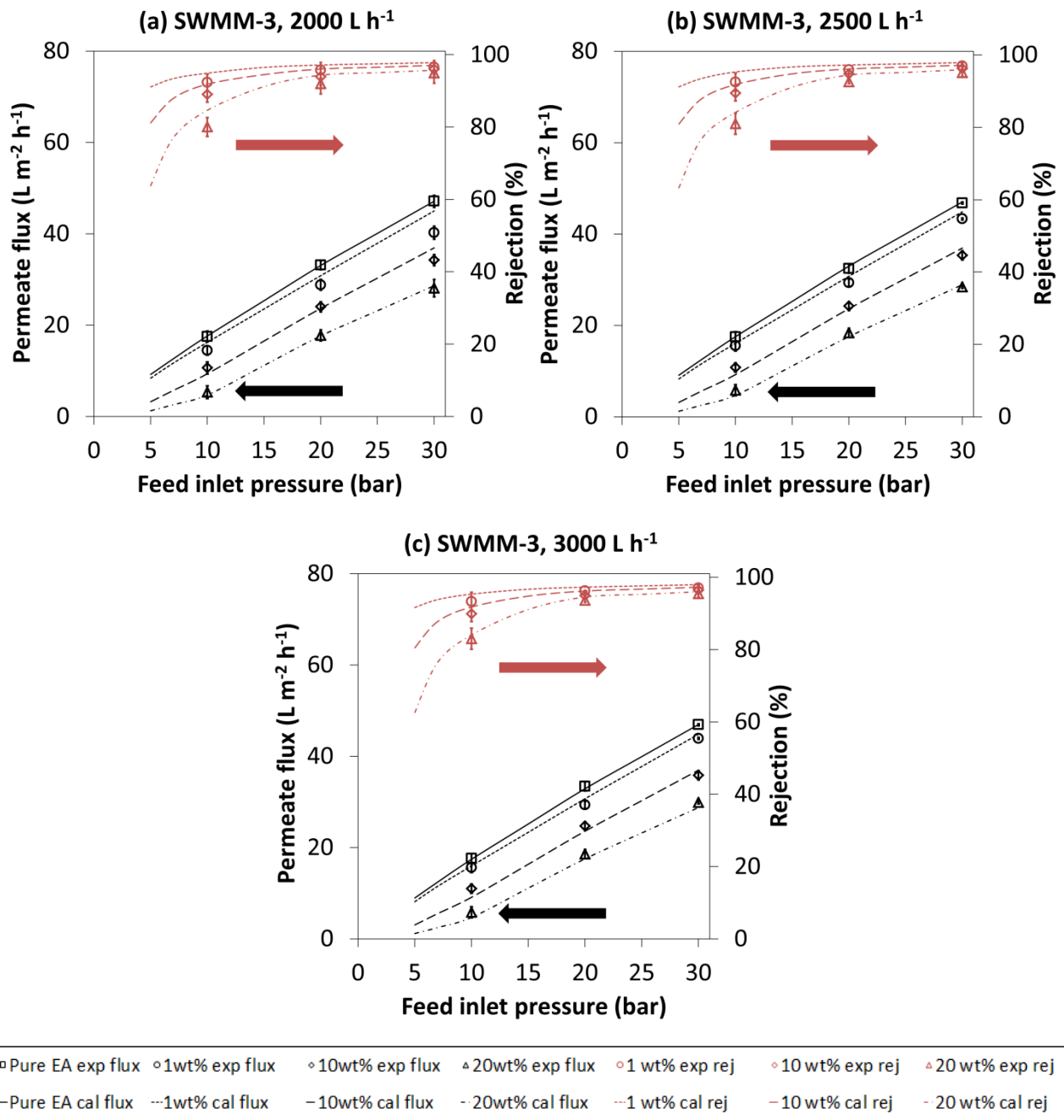


Figure 3.14: Experimental and calculated flux (black) and rejection (red) of the 4.0"x40" SWMM-3 module tested in 0 – 20 wt% SoA in EA solutions at 30 °C and various pressures (10, 20 and 30 bar) with different retentate flowrates: (a) 2,000 L h⁻¹; (b) 2,500 L h⁻¹; (c) 3,000 L h⁻¹. The performance of the 4.0"x40" SWMM-3 module was not used in the regression procedure. Rather, the regressed parameters were used to simulate the performance of this module and validate the model by comparing to experimental data.

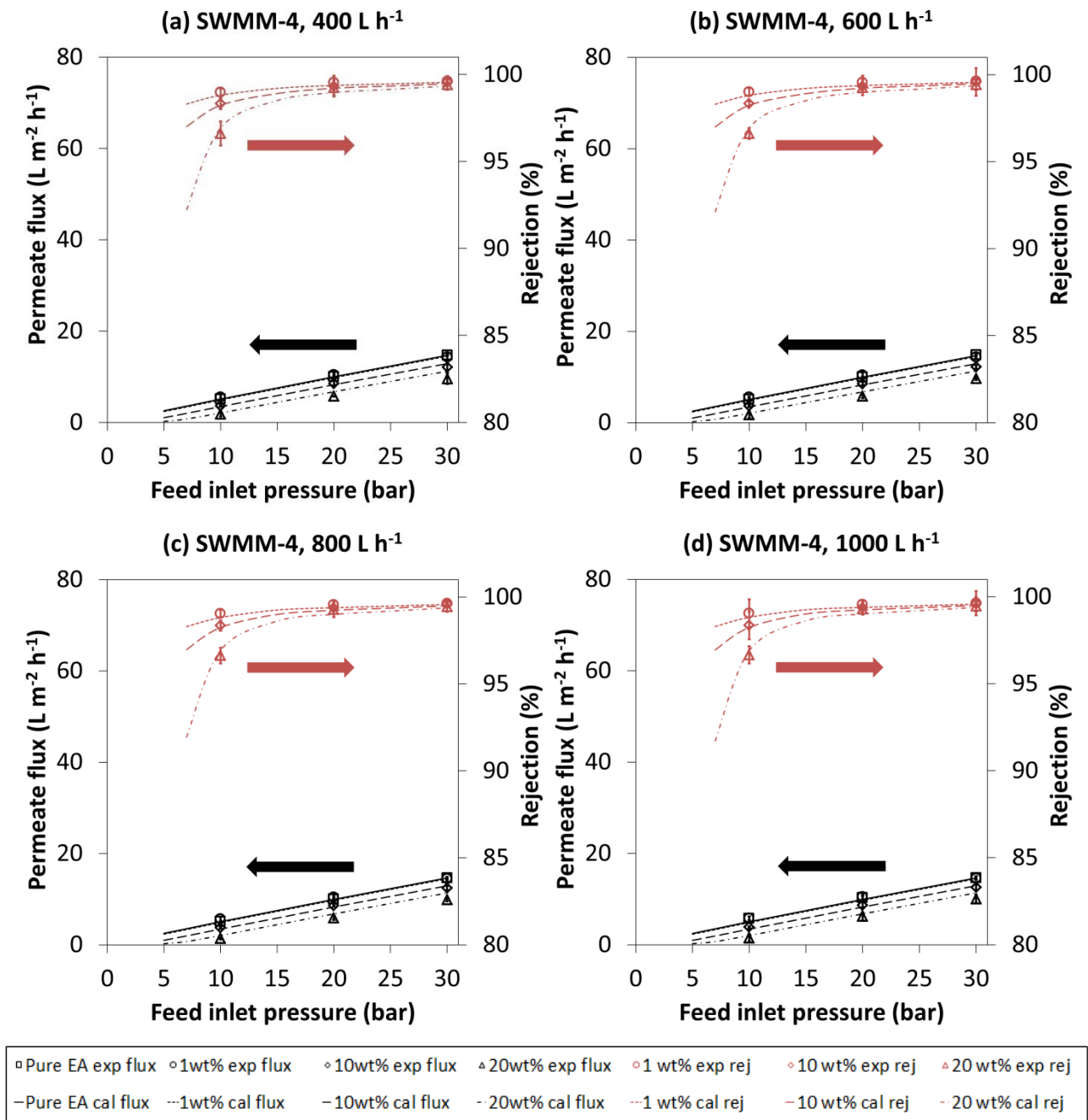


Figure 3.15: Experimental and calculated flux (black) and rejection (red) of the 2.5"x40" SWMM-4 module tested in 0 – 20 wt% SoA in EA solutions at 30 °C and various pressures (10, 20 and 30 bar) with different retentate flowrates: (a) 400 L h⁻¹; (b) 600 L h⁻¹; (c) 800 L h⁻¹; (d) 1,000 L h⁻¹. The performance of the 2.5"x40" SWMM-4 module was not used in the regression procedure. Rather, the regressed parameters were used to simulate the performance of this module and validate the model by comparing to experimental data.

Figure 3.16 shows that the mass transfer coefficient in these three modules (SWMM-2, SWMM-3 and SWMM-4) has an order of magnitude of 10⁻⁵ m s⁻¹, similar to the SWMM-1 module (see Figure 3.11).

Although these modules have longer feed channels with respect to the SWMM-1 module, the mass transfer coefficients did not change significantly along the feed channel.

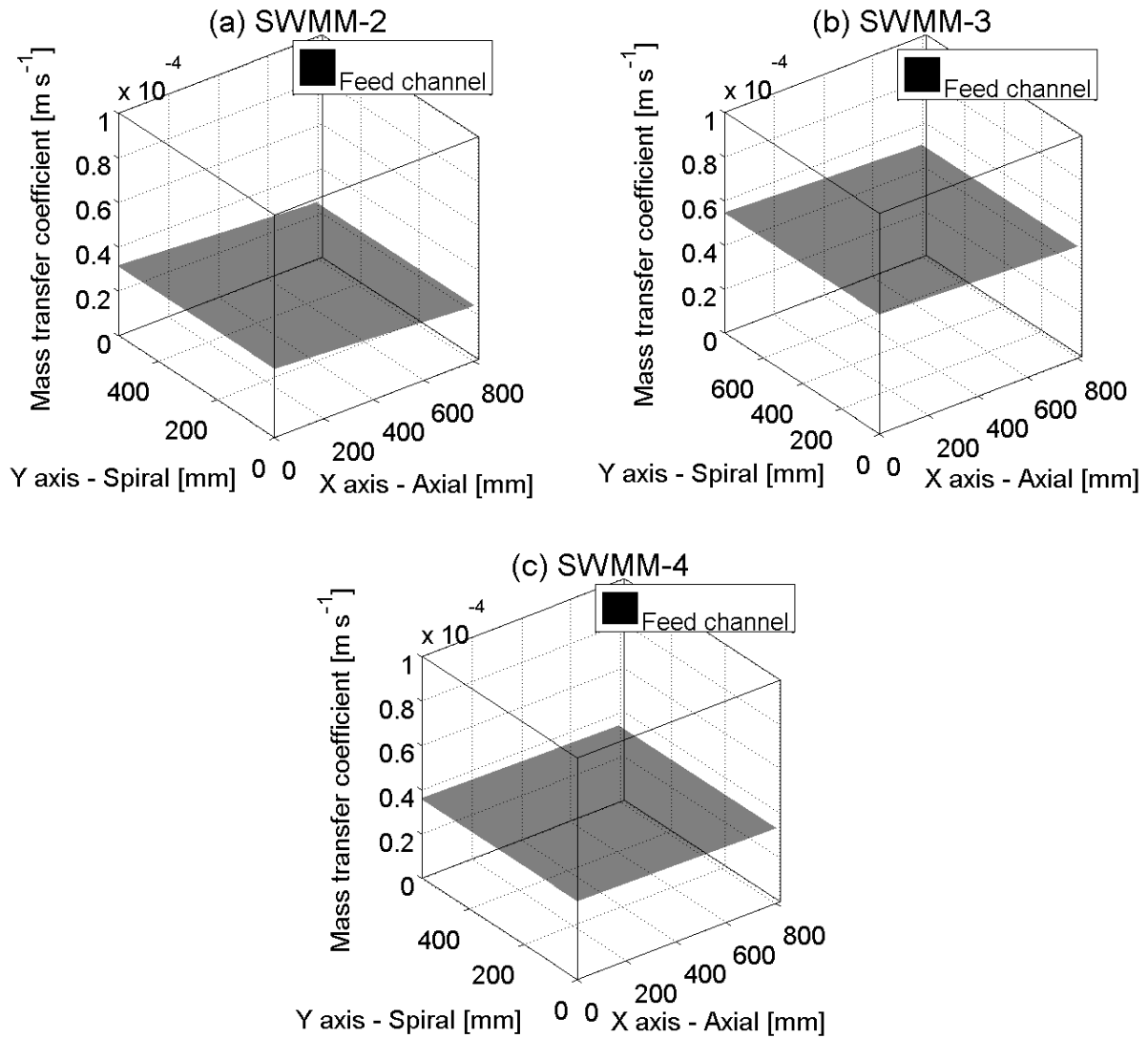


Figure 3.16: Profiles of mass transfer coefficients in the feed channel of the different modules in 1 wt% SoA in EA solution at 30 bar and 30 °C with different retentate flowrates. (a) SWMM-2 module with a retentate flowrate of 300 L h⁻¹; (b) SWMM-3 module with a retentate flowrate of 2,000 L h⁻¹; (c) SWMM-4 module with a retentate flowrate of 400 L h⁻¹.

Finally, these results show that the empirical correlations determined from the regression of data from the smallest module (SWMM-1, 1.8"x12") can be used to accurately predict the fluid dynamics and mass transfer characteristics in other modules, which have larger sizes and/or are made of a different membrane

material. They further show that the performance of a SWMM can be predicted from simple flat sheet laboratory measurements, as long as the fluid dynamics and mass transfer characteristics in the SWMM are known. In this work, the Reynolds number in the feed channel was between 45 and 600; the Schmidt number in the feed channel was between 200 and 440; and the Reynolds number in the permeate channel was lower than 22. The correlations obtained in this work could be used to describe the fluid dynamics and mass transfer characteristics in any spiral-wound membrane module which is fabricated with the same feed and permeate spacers, and used in the applications where Reynolds and Schmidt numbers are in a similar range, as mentioned above.

3.5 Conclusions

This chapter reports the performance of four spiral-wound membrane modules tested in 0 – 20 wt% solutions of SoA in EA under various pressures and retentate flowrates. These modules were made with two different types of membranes (a commercial membrane, PuraMem® S600, and a development product, Lab-1, from EMET) and covered three module sizes (1.8"x12", 2.5"x40" and 4.0"x40"). All modules had the same feed and permeate spacers (referred to as EMET-F3 and EMET-P1, respectively). Initially the effects of time and pressure on flat sheet membranes were investigated. The permeance through both membranes was almost independent of the pressure, while the rejection was positively affected by the pressure: the higher the pressure, the higher the rejection. Moreover, the membrane performance (in terms of both flux and rejection) showed negligible change after the membrane was compressed at high pressure, indicating that these membranes did not undergo any significant irreversible compaction.

The classical SD model was selected to describe the transport through the membrane. The unknown model parameters were determined from regression of experimental flat sheet data at one unique pressure value. These parameters were then used to predict the performance of the flat sheet membranes under different pressures and good agreement was observed for both types of membranes (PM S600 and Lab-1). This

indicated that the classical SD model was adequate to describe the transport through the membranes in this study. A correlation to characterise the friction coefficient in the feed channel was determined by regression of the feed pressure drop data through the 1.8"x12" (SWWM-1) module. During the same regression procedure, the parameters describing the feed channel, necessary to calculate the Reynolds number, were also obtained. These fitting parameters were then used to predict the feed pressure drops in the other three modules and good agreement was observed between calculated and experimental data. A similar correlation for the friction coefficient in the permeate channel and a correlation for the mass transfer coefficient in the feed channel were determined by regression of the 1.8"x12" performance data (in terms of both flux and rejection). Here the classical SD model combined with the film theory was used, with the consideration of the gradients of concentration, pressure, velocity and mass transfer coefficient through the module. The parameters describing the permeate channel were also obtained in the same regression procedure.

The three empirical correlations thus obtained, for the friction coefficients in the feed and permeate channels and the mass transfer coefficient in the feed channel, respectively, were used to predict the performance of all other modules used in this study. Good agreement was observed, which proves that the empirical correlations determined from the regression of the smallest module (1.8"x12") can be extended to describe the fluid dynamics and mass transfer characteristics in other modules, which have larger sizes and/or are made of different membranes. The correlations obtained in this work could be used to describe the fluid dynamics and mass transfer characteristics in any spiral-wound membrane module which is fabricated using the same feed and permeate spacers, and used in the applications where (i) Reynolds number in feed channel is in the range between 45 and 600; (ii) Schmidt number in feed channel is between 200 and 440; and (iii) Reynolds number in permeate channel is lower than 22.

3.6 Acknowledgements

This chapter is reproduced from my own published paper (<http://dx.doi.org/10.1016/j.memsci.2015.07.044>). It is with permission from 'B. Shi, P. Marchetti, D. Peshev, S. Zhang, A.G. Livingston, Performance of spiral-wound membrane modules in organic solvent nanofiltration – fluid dynamics and mass transfer characteristics, J. Membr. Sci., 494, 8 – 24, Elsevier 2015'.

Chapter 4

Multi-scale modelling of OSN batch concentration with spiral-wound membrane modules using OSN Designer

4.1 Introduction

Primarily, research activities in the field of OSN have been focused on the development of new materials stable in organic solvents and harsh conditions, while industrial scale applications are still few. A fundamental understanding of the basic separation mechanism and a reliable modelling framework are crucial to bridge this gap, meet the growing needs and applications, and make scale-up more efficient and economic [29]. In the development of a multi-scale mathematical model for an OSN process with SWMMs, the following problems have to be resolved: (i) selection of adequate membrane transport mechanism to describe the molecular transport across the membrane; (ii) knowledge of the fluid dynamics and mass transfer characteristics in the module; (iii) availability of the thermodynamic and physical properties of the solutions under different operating conditions. The first two problems have been discussed in Chapters 2 and 3. Specifically, the classical SD model has been proven to be able to predict the performance of the rubber membranes (PM S600 and Lab-1) in SoA / EA solutions, whilst the friction coefficient and Sherwood number correlations were developed for describing the fluid dynamics and mass transfer characteristics in the SWMMs made of the EMET-F3 and EMET-P1 spacers in SoA / EA solutions.

In this chapter, the performance of a process to concentrate SoA / EA solutions using three commercial spiral-wound PM S600 membrane modules of different sizes, from 1.8"x12" to 4.0"x40", in batch operation was experimentally investigated. Furthermore, a process model implemented via "OSN Designer" was developed. In this process model, a unit membrane operation was programmed in MATLAB, considering molecular transport through membranes, and fluid dynamics and mass transfer characteristics in the SWMMs. The MATLAB programme can communicate with process models such as Aspen Plus, HYSYS and ProSim Plus via Cape Open. In this way, the thermodynamic and physical properties of the solutions can be simulated using built-in models in process models, as a function of operating conditions. As in this chapter, the thermodynamic and physical properties of SoA / EA solutions were calculated using the UNIFAC-DMD method in Aspen Plus. Good agreement between experiments and simulation showed the potential of applying this approach to predict the performance of any OSN process which uses SWMMs, based on simple flat sheet test data. In addition, the effects of concentration polarisation, pressure drops through feed and permeate channels and thermodynamic non-ideality of the solution at large scale batch concentration are also investigated.

4.2 Materials and methods

4.2.1 Materials

Analytical grade EA was purchased from Tennants Distribution Limited, UK. SoA (>97% purity) was purchased from Sigma Aldrich Limited, UK. The high solubility of SoA in EA makes this binary system appropriate for the present study, since it allows relatively high concentration to be achieved. The solution has the same components as the one used in Chapter 3.

Three spiral-wound PuraMem® S600 membrane modules were provided by EMET, covering three sizes: 1.8"x12", 2.5"x40" and 4.0"x40". These three modules are the same PM S600 membrane modules used in Chapter 3. The configuration of these three modules are shown in Table 3.1.

4.2.2 Experimental methods

In this chapter, the three commercial modules were operated in batch concentration mode using three different experimental rigs. The 1.8"x12" module (SWMM-1) and 2.5"x40" module (SWMM-2) were incorporated in a single-pump system, which is schematically represented in Figure 3.2(b). The SWMM-1 module was operated using a single diaphragm pump (Hydra-Cell D3) and the retentate flowrate was controlled between 80 and 240 L h⁻¹. The SWMM-2 module was operated using a more powerful diaphragm pump (Hydra-Cell D10), capable of controlling the flowrate from 300 to 900 L h⁻¹, in order to supply sufficient feed linear velocity through the module. The 4.0"x40" module (SWMM-3) module was incorporated in a two-pump rig as shown in Figure 3.2(c). Compared to the single-pump rig, the two-pump rig including a diaphragm pump (Hydra-Cell D10) and a circulation pump (Peripheral-Pump HMM125) was able to provide sufficient cross-flow velocity through the feed channel of the module. After the Flow Indicator 1, a fraction of the retentate circulates through the module with a high flowrate, forming an inner circulation loop (Heat Exchanger → Circulation Pump 1 → Pressure Indicator 1 → Module Housing → Pressure Indicator 2 → Flow Indicator 1 → Heat Exchanger). The remaining fraction of the retentate flows back through the back pressure valve to the feed tank (recycle fraction). The feed flowrate through the module in the inner circulation loop was controlled between 1,000 and 3,000 L h⁻¹ and the fluid flowrate after the back pressure valve was controlled to be around 85 ± 11 L h⁻¹. In the batch concentration process, the permeate was collected in a separate container and weighed in a balance (not shown in Figures 3.2(b) and (c)). A summary of the operating conditions of the batch concentration operation with the three different modules is reported in Table 4.1. All modules were washed using pure EA and operated in the initial solution for 6 hours at steady state operation before switching to the batch concentration operation.

Table 4.1: Operating conditions of the batch concentration with different spiral-wound membrane modules

Entry	Module	Initial feed volume (L)	Initial feed concentration (wt %)	Temperature (°C)	Pressure (bar)	Retentate flowrate (L h ⁻¹)	Process time (min)
1	1.8"x12"	6	3.9	30	10	80	110
2	1.8"x12"	6	3.9	30	10	240	110
3	1.8"x12"	6	3.9	30	30	80	40
4	1.8"x12"	6	3.9	30	30	240	40
5	2.5"x40"	80	2.5	30	10	300	150
6	2.5"x40"	80	2.5	30	10	900	150
7	2.5"x40"	80	2.5	30	30	300	50
8	2.5"x40"	80	2.5	30	30	900	50
9	4.0"x40"	80	6	30	10	1,000	70
10	4.0"x40"	80	6	30	10	3,000	70
11	4.0"x40"	80	6	30	30	1,000	20
12	4.0"x40"	80	6	30	30	3,000	20

The performance of the membrane batch concentration operations was characterised by three parameters: the change of the volume of the feed solution, the change of the solute concentration in the tank and the percentage loss of the solute to permeate, all over time. The volume of the feed solution at each time t , $V_{f,t}$, is calculated as the difference between the volume of the initial feed solution, $V_{f,0}$, and the cumulative permeate volume, $V_{p,t}$. This is shown in Equation (4.1). The permeate was collected in a separate container and the weight was measured over time using balance with a capacity of 20 kg for the SWMM-1 module and 200 kg for both the SWMM-2 and SWMM-3 modules. The accuracy is ± 0.1 g for the SWMM-1 module and ± 10 g for both the SWMM-2 and SWMM-3 modules. The volume of permeate was then calculated using the density of the solution which was obtained from concentration analysis of a permeate sample taken from the permeation collection tank at the same time point. The feed samples

were also taken at discrete times for analysing the solute concentration in the tank, and its change over time. The percentage loss of solute to permeate at time t , $L_{s,t}$, in the feed tank was calculated using Equation (4.2). $C_{f,s,0}$ is the initial solute concentration in the feed and $C_{p,s,t}$ is the solute concentration in the permeation collection tank at process time t .

$$V_{f,t} = V_{f,0} - V_{p,t} \quad \text{Equation (4.1)}$$

$$L_{s,t} = \frac{V_{p,t} \cdot C_{p,s,t}}{V_{f,0} \cdot C_{f,s,0}} \quad \text{Equation (4.2)}$$

The concentration of SoA was determined using a gas chromatograph with a flame ionisation detector and a fused silica column (Rtx[®] – 2887 column purchased from Thames Restek Limited, UK), as specified in the section 3.2.2.3.

4.2.3 Modelling

The modelling in this chapter was carried out using the OSN Designer software tool where all thermodynamic and physical properties of the solutions were obtained using the Aspen Properties Estimate system with the Dortmund modified UNIFAC (UNIF-DMD) as a base method in the Aspen Plus V7.3 environment, as specified in the section 3.3.1. A mathematical model for the batch concentration operation considering the gradients of concentration, pressure and velocity through the module, the concentration polarisation and the thermodynamic non-ideality of the solutions was programmed in MATLAB, which communicates with Aspen Plus via the CAPE OPEN interface, as shown in Figure 4.1.

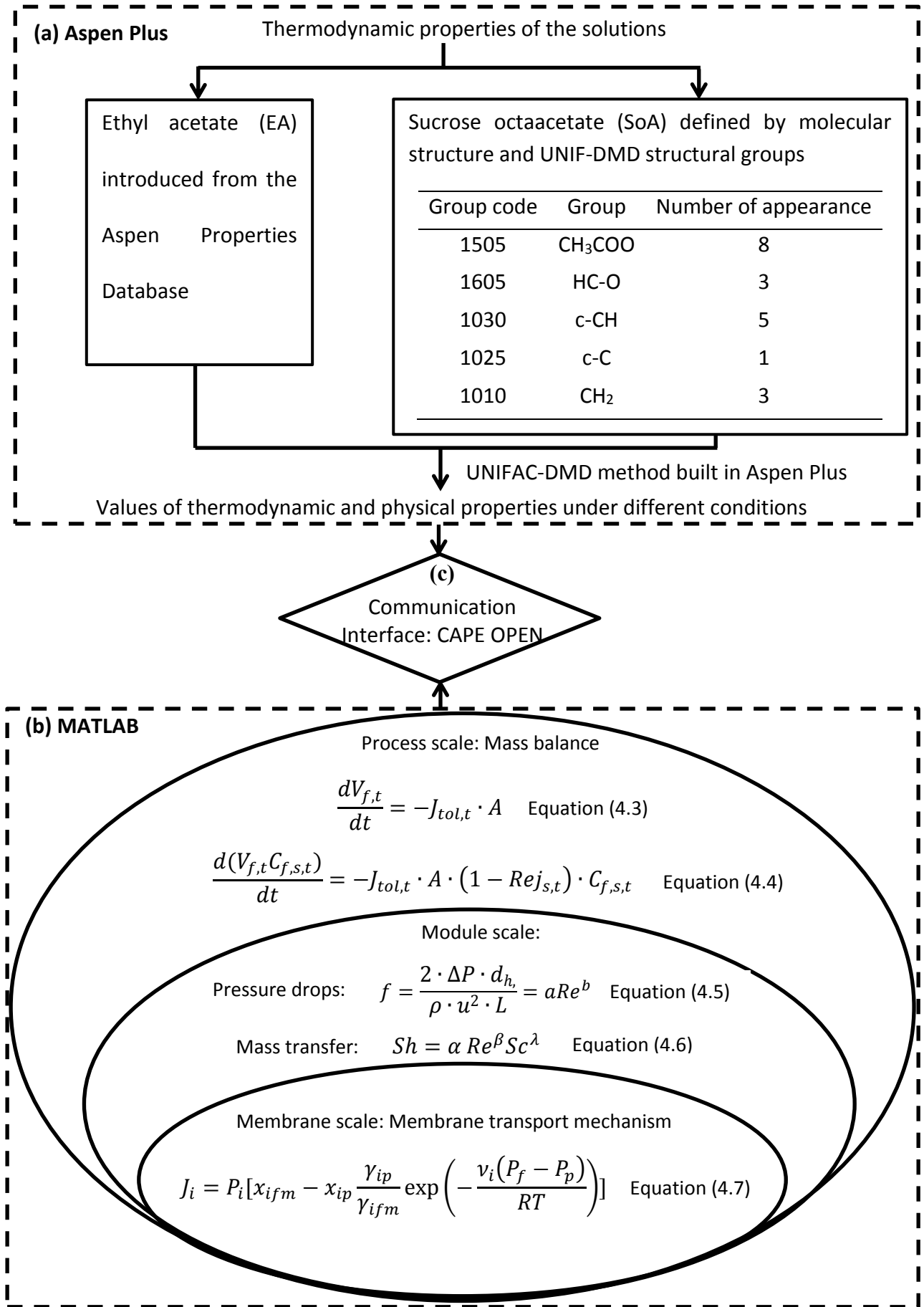


Figure 4.1: Schematic representation of the OSN Designer software used to simulate the batch concentration operations in this chapter. (a) Calculation of the thermodynamic properties of the solutions using UNIFAC-DMD model in Aspen Plus; (b) multi-scale modelling of the batch concentration unit operation at membrane, module and process scales in MATLAB; (c) CAPE OPEN interface for communication between Aspen Plus and MATLAB.

As shown in Figure 4.1(a), EA was available from the database in Aspen Plus while SoA is defined using UNIFAC-DMD structural groups since it is not available in the Aspen Properties Database, as specified in section 3.3.1. The material balance equations for the entire batch concentration operation are represented by Equations (4.3) and (4.4) (see Figure 4.1(b)). A is the effective membrane area in the module. $J_{tol,t}$ and $Rej_{s,t}$ are the permeate flux and rejection at process time t , respectively. It is assumed that the solution in the feed tank is well mixed and the time consumed for the retentate circulation is negligible. The flux and rejection through the module are calculated using the combination of the classical SD model and the film theory discussed in the chapter 3, as shown in Equation (4.7) (see Figure 4.1(b)). The effects of the pressure drop through both the feed and permeate channels and the mass transfer were considered by using the friction coefficient and Sherwood number correlations developed in the chapter 3, shown as Equations (4.5) – (4.6) (see Figure 4.1(b)). In this chapter, the model parameters and correlations obtained from regression of experimental data in steady state mode in the chapter 3 are used to predict the performance of batch concentration, since the SWMMs are made of the same membranes and spacers, and tested in the solutions containing the same components, and Reynolds and Schmidt numbers are within the valid range. The membrane transport properties, feed and permeate channel geometry, fluid dynamics and mass transfer characteristics are summarised in Table 4.2. Besides, the permeate flux, $J_{tol,t}$ and the solute rejection, $Rej_{s,t}$, are defined as Equations (4.8) and (4.9), respectively.

$$J_{tol,t} = \frac{F_{p,t}}{A} \quad \text{Equation (4.8)}$$

$$Rej_{s,t} = \left(1 - \frac{C_{p,s,t}}{C_{r,s,t}}\right) \cdot 100\% \quad \text{Equation (4.9)}$$

$F_{p,t}$ is the permeate flowrate at process time t and $C_{r,s,t}$ is the concentration of the solute in the retentate at process time t .

Table 4.2: Summary of the model parameters required to simulate the batch concentration processes (taken from Chapter 3: membrane transport properties, feed and permeate channel geometry, fluid dynamics and mass transfer characteristics)

Membrane	Solute permeability coefficient (mol m ⁻² s ⁻¹)	2.06E-3
	Solvent permeability coefficient (mol m ⁻² s ⁻¹)	1.59
Feed channel	Height (mm)	0.77
	Void fraction (-)	0.827
	Hydraulic diameter (mm)	0.79
	Friction coefficient correlation	$f_f = 6.94 Re_f^{-0.34}$
	Sherwood number correlation	$Sh_f = 0.075 Re_f^{0.61} Sc_f^{0.33}$
Permeate channel	Height (mm)	0.27
	Void fraction (-)	0.315
	Hydraulic diameter (mm)	0.048
	Friction coefficient correlation	$f_p = 16 Re_p^{-0.34}$

In addition, in the development of a new OSN process, the first step is usually to screen the membranes in cross-flow cells and then to prove that the chosen membrane performs well in a small 1.8"x12" module before scale-up. Therefore, even for a different application using different modules, the experimental data (both flat sheets and a 1.8"x12" module) are usually available a priori, to obtain the model parameters using the procedure developed in Chapter 3.

4.3 Results and discussion

Figures 4.2 – 4.4 show the performance of the batch concentration operations with different commercial spiral-wound membrane modules of different sizes (1.8"x12", 2.5"x40" and 4.0"x40", respectively) under various retentate flowrates and feed pressures in SoA / EA solutions. The feed solutions were concentrated three to seven times from relatively low concentration (2.5 – 6 wt%) to high concentration (12 – 21 wt%). For all three modules, it can be seen that the volume in the feed tank decreases and the solute concentration in the feed tank increases over time. Furthermore, increasing the feed pressure can accelerate the batch concentration process due to the increase in the permeate flux: in Figures 4.2-4.4(a,b), obtained at 10 bar, the process is completed in 110, 150 and 70 minutes for SWMM-1, SWMM-2 and SWMM-3, respectively, while in Figures 4.2-4.4(c,d), obtained at 30 bar, the process time is completed in 40, 50 and 22 minutes, respectively. The retentate flowrate has also a positive effect on the concentration process: in Figures 4.2-4.4(a,c), obtained at low retentate flowrate, the process time is 2 - 7 minutes longer than at high retentate flowrate in Figures 4.2-4.4(b,d). This occurs because high retentate flowrate reduces the concentration polarisation, increases the permeation flux and thus makes the concentration process faster.

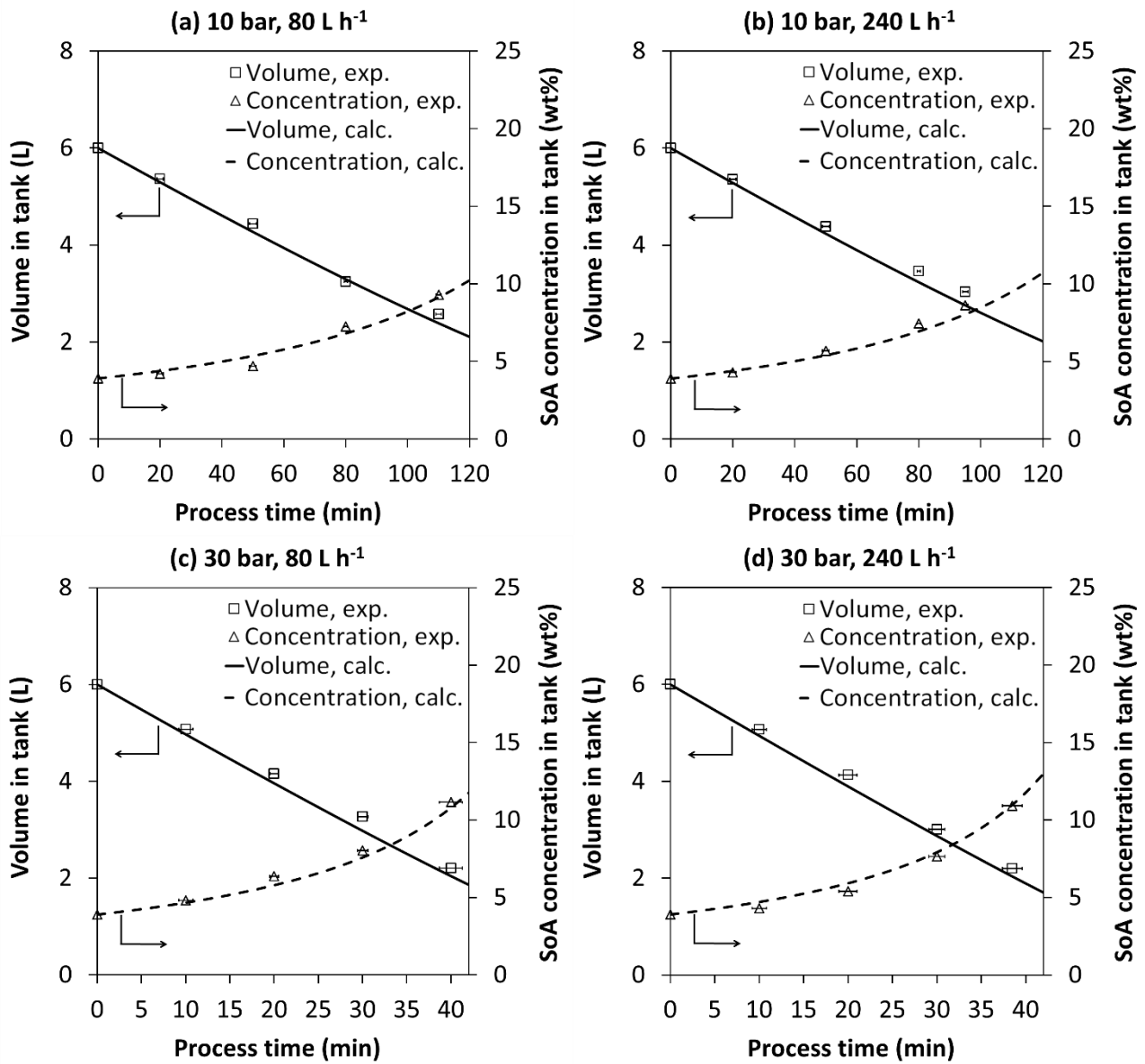


Figure 4.2: Experimental (exp.) and calculated (calc.) performance of the batch concentration process over time with a 1.8"x12" spiral-wound PuraMem® S600 membrane module tested at 30 °C with various feed pressures and retentate flowrates (Entries 1 – 4 in Table 4.1). The error bars on the x-axis indicate the time spent to take the samples and record the data.

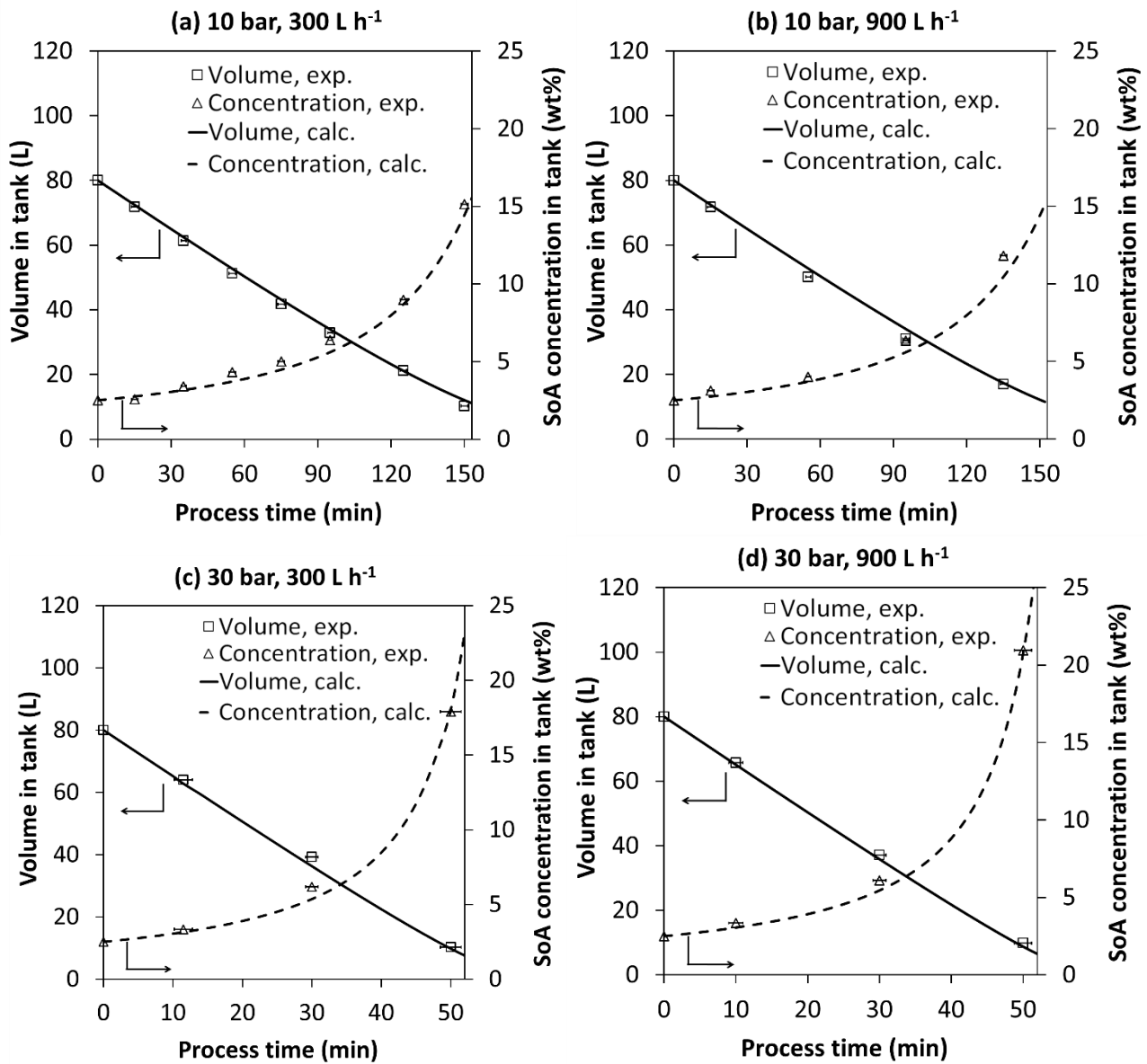


Figure 4.3: Experimental (exp.) and calculated (calc.) performance of the batch concentration process over time with a 2.5"x40" spiral-wound PuraMem® S600 membrane module tested at 30 °C with various feed pressures and retentate flowrates (Entries 5 – 8 in Table 4.1). The error bars on the x-axis indicate the time spent to take the samples and record the data.

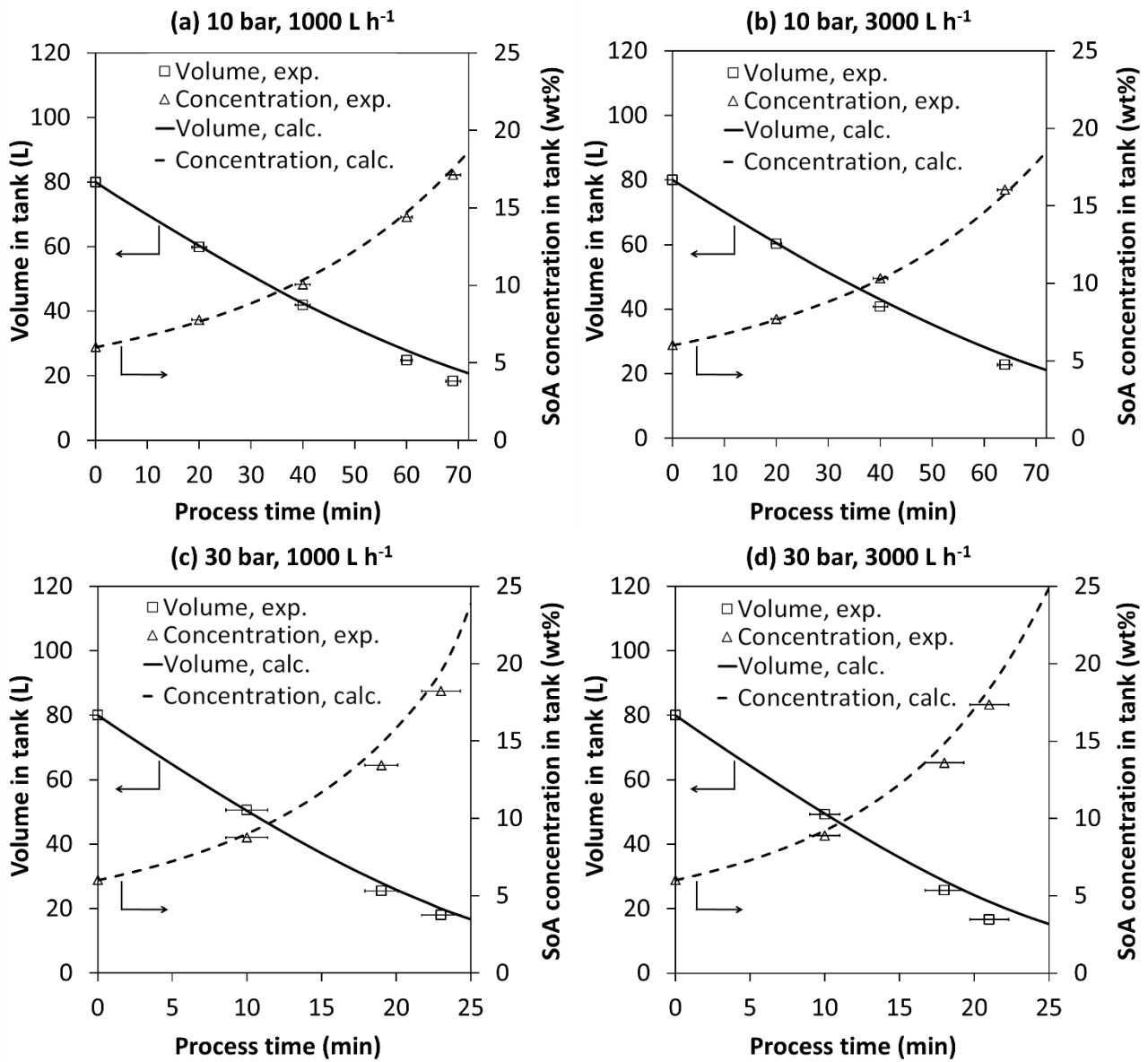


Figure 4.4: Experimental (exp.) and calculated (calc.) performance of the batch concentration process over time with a 4.0"x40" spiral-wound PuraMem® S600 membrane module tested at 30 °C with various feed pressures and retentate flowrates (Entries 9 – 12 in Table 4.1). The error bars on the x-axis indicate the time used to take the samples and record the data.

For all three module sizes, very good agreement was observed between the experimental and simulated module performance (see Figures 4.2 – 4.4). This indicates that the performance of the batch concentration process with spiral-wound membrane modules can be predicted from laboratory cross-flow flat sheet data when both the fluid dynamics and mass transfer characteristics and necessary geometry for spacer-filled

channels in the modules are known. Moreover, the success of this approach in predicting the performance of the batch concentration shows the potential for using it in other OSN processes. The OSN Designer tool provides the all necessary thermodynamic and physical properties of various solute/solvent combinations, as a function of operating conditions.

In industrial membrane concentration processes, such as the recovery of a valuable compound in the pharmaceutical industry, or the recovery of solvents in the chemical industry, often the membrane rejection is high but not total (100 %) [14]. In this case it is very important to control the loss of solute to permeate during the process. Besides the intrinsic membrane rejection, the fluid dynamics in the module has an effect on the loss of solute to permeate too. Figure 4.5 shows the percentage loss of SoA to permeate during the batch concentration processes studied in this chapter under various operating conditions. It is clear that the increase in the retentate flowrate effectively reduces the loss of solute to permeate. This is due to a decrease in the concentration polarisation and an increase in the solute rejection at high retentate flowrates. This effect is more obvious when the concentration of the solution is high (represented by the increasing relative difference between the performance at low and high retentate flowrates in Figures 4.5(a-c)). Besides, in this study increasing the feed pressure reduced the solute loss to permeate, represented by the relative difference between the performance at low and high pressures in Figures 4.5. It is due to the fact that the ratio of solute flow to permeate to solvent flow to permeate (solute concentration in permeate) reduced when the feed pressure increased from 10 bar to 30 bar, resulting in higher rejection, according to the simulation data. This trend was also observed in the experiments with the same membrane modules in SoA/EA solutions in a steady-state operation in Chapter 3.

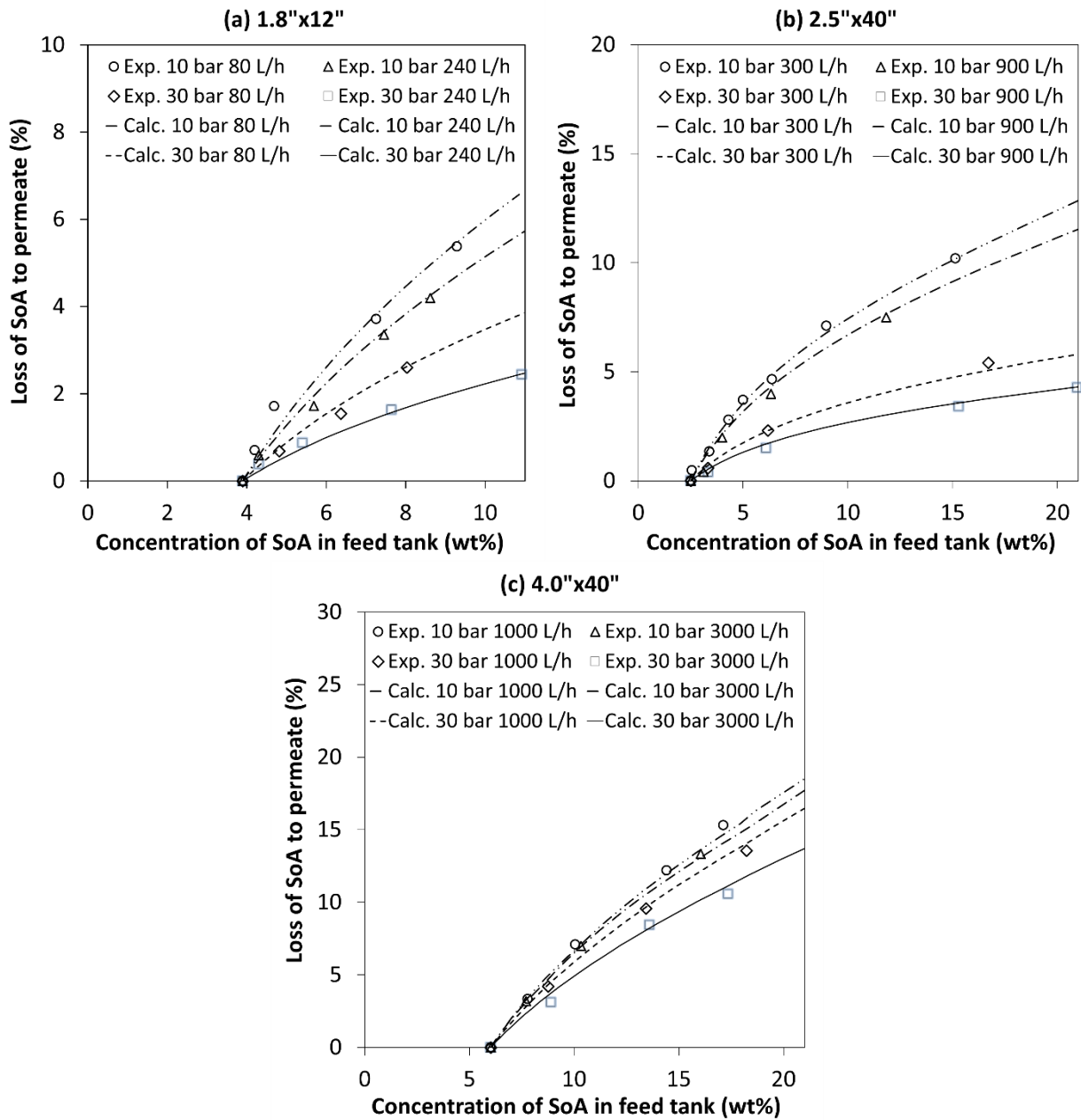


Figure 4.5: Experimental (exp.) and calculated (calc.) percentage loss of the solute to permeate in the batch concentration process under various retentate flowrates and feed pressures at 30°C with three different commercial spiral-wound membrane modules: (a) 1.8"x12" spiral-wound membrane module; (b) 2.5"x4.0" spiral-wound membrane module; (c) 4.0"x40" spiral-wound membrane module.

Although increasing the feed pressure accelerates the process and reduces the loss of solute to permeate, increasing the feed pressure can damage the membrane when the feed pressure exceeds the maximum pressure the membrane can tolerate. Moreover, the increase of the membrane flux causes increases of the

pressure drop in the permeate channels. This strongly limits the benefit of having a higher flux from increasing the feed pressure. Similarly, the benefit of increasing the retentate flowrate on the concentration process has the drawback of requiring higher energy consumption. Besides, the increase of the retentate flowrate may cause telescoping and even damage the modules. In conclusion, during the process design, the optimal value of the feed pressure and retentate flowrate for a specific application has to be identified, in terms of process efficiency, solute recovery and energy consumption.

Figure 4.6 shows the importance of considering feed and permeate pressure drop in the simulation of volume reduction and solute concentration after 10 minutes of operation (see Figure 4.6(a)) and after 50 minutes of operation, i.e. at the end of the process (see Figure 4.6(b)). The simulation was carried out accounting for the friction coefficients in both feed and permeate channels (entry “Both feed and permeate pressure drop” in Figure 4.6), as well as by accounting for pressure drop in the permeate channel only (entry “Only permeate pressure drop” in Figure 4.6) or accounting for the pressure drop in the feed channel only (“Only feed pressure drop” in Figure 4.6). The gradients of concentration and velocity through both feed and permeate channels, the concentration polarisation and the thermodynamic non-ideality of the solution were considered in all the cases. Very good agreement between the experiments and the calculation was obtained when both feed and permeate pressure drop were taken into consideration. It can be seen that when the permeate pressure drop only is considered in the model, there is also good agreement between experimental and calculated data, although the accuracy is slightly lower. This is due to the negligible feed pressure drop in this specific case study (< 0.5 bar). In industrial applications where several modules are connected in series, however, the feed pressure drop may become important. The impact of the permeate pressure drop on both volume and concentration is almost negligible at the beginning of the process (see Figure 4.6(a)) and much more significant at the end of the process (see Figure 4.6 (b)). This suggests that the pressure drop through the permeate channel of the module must be known, in order to accurately predict the performance of the batch concentration process using spiral-wound membrane modules.

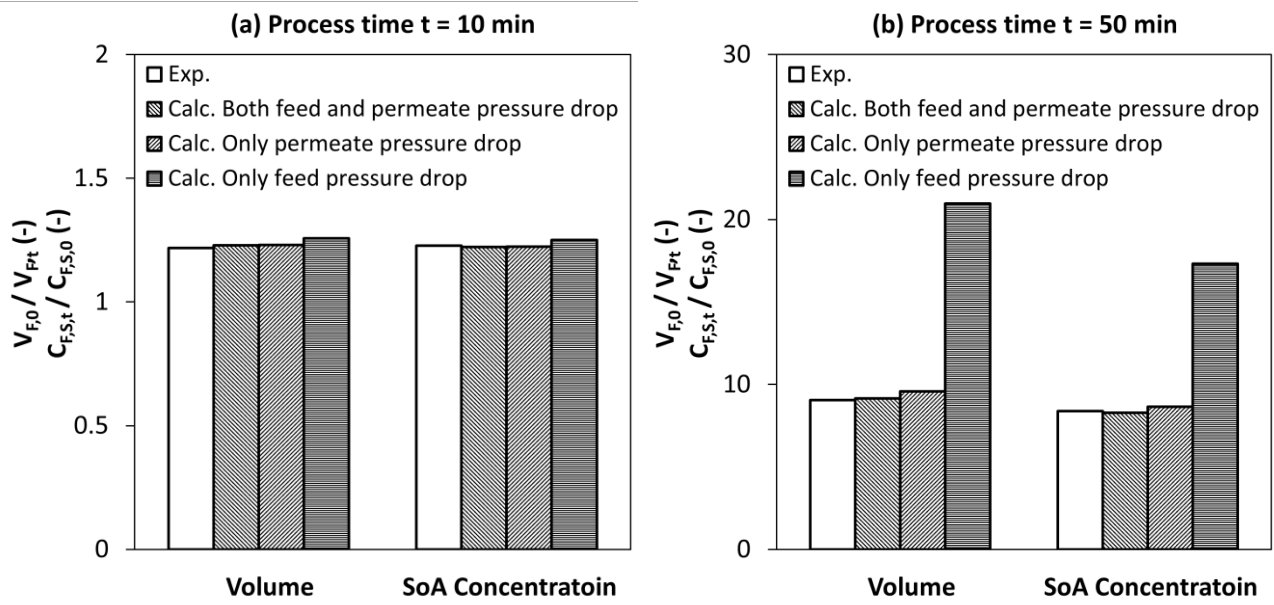


Figure 4.6: Experimental (exp.) and calculated (calc.) normalised volume and solute concentration during the batch concentration process of sucrose octaacetate in ethyl acetate with the 2.5"x40" spiral-wound membrane module and effect of feed and permeate pressure drop at different process times: (a) 10 minutes and (b) 50 minutes. The process was run at 30 °C and 30 bar with a retentate flowrate of 900 L h⁻¹. Volume and solute concentration were normalised with respect to the initial solution volume ($V_{f,0}$) and solute concentration ($C_{f,s,0}$).

The effects of concentration polarisation on the performance of the batch concentration process with the 2.5"x40" spiral-wound membrane module are shown in Figure 4.7. To simulate the absence of concentration polarisation, the simulation was carried out assuming a very large Sherwood number (of 10^{36}). At the beginning of the process (11.5 minute, see Figure 4.7(a)), the difference between the simulation with and without accounting for the concentration polarisation was negligible and good agreement with the experimental data was observed. This is due to the relatively low concentration of the feed solution at the beginning of the process (< 10 wt%). On the other hand, the effect of concentration polarisation becomes important when the feed concentration is high. In fact, the calculation considering concentration polarisation showed good agreement with the experimental data while the one neglecting the concentration polarisation showed a deviation of 35%.

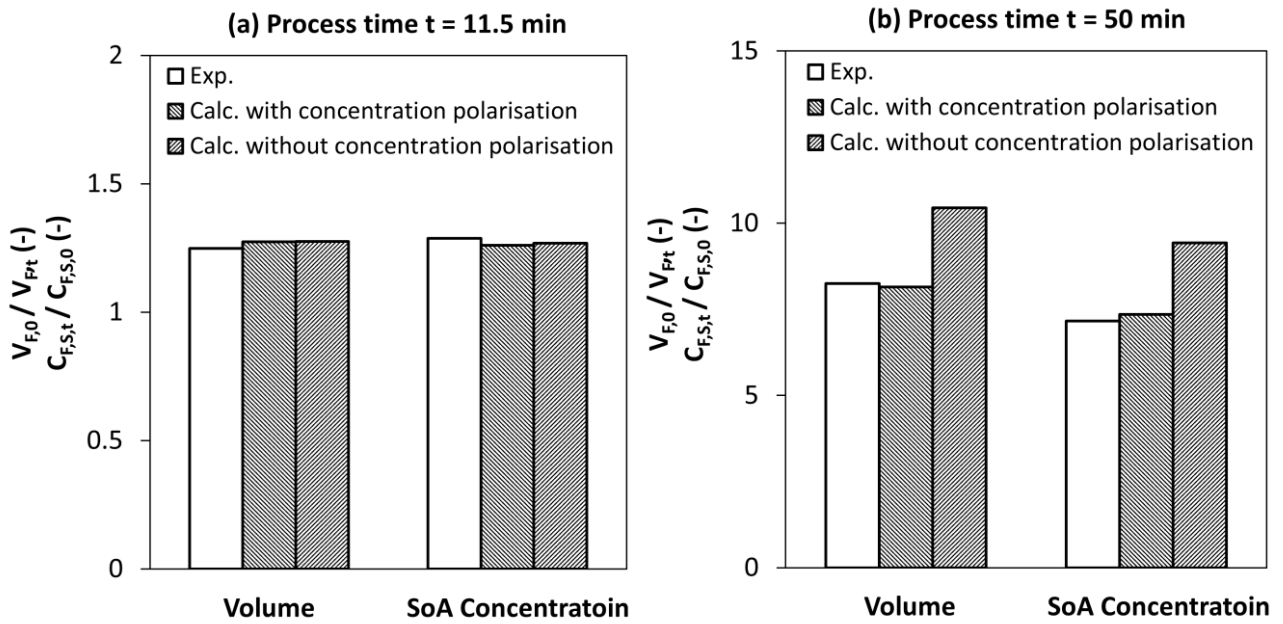


Figure 4.7: Experimental (exp.) and calculated (calc.) normalised volume and solute concentration during the batch concentration process of sucrose octaacetate in ethyl acetate with the 2.5"x40" spiral-wound membrane module and effect of concentration polarisation at different process times: (a) 11.5 minutes and (b) 50 minutes. The process was run at 30 °C and 30 bar with retentate flowrate of 300 L h⁻¹. Volume and solute concentration were normalised with respect to the initial solution volume ($V_{f,0}$) and solute concentration ($C_{f,s,0}$).

A third factor, which has impact on the process performance, is the thermodynamic non-ideality of the solution. Therefore, a simulation of batch concentration process with the 2.5"x40" spiral-wound membrane module was performed in order to assess the importance of this factor. The results are shown in Figure 4.8. The simulations were carried out accounting for the activity coefficient of both solute and solvent (entry "Gamma = UNIFAC-DMD") or assuming that the activity coefficient of both solute and solvent was 1 (entry "Gamma = 1"). The difference between the simulations with and without accounting for the thermodynamic non-ideality of the solutions at the beginning of the process (11.5 minute) was negligible, and good agreement with the experimental data was observed. This can be explained by the relatively low deviation from the ideal behaviour at initial concentration (<10 wt%). On the other hand, the effect of solution non-ideality became important at the end of the process (50 minutes, see Figure 4.8(b)) when the

feed concentration was high (about 18 wt%). The simulation considering ideal solution underestimated the performance of about 13%. These results indicate that thermodynamic non-ideality has significant impact on the process performance when highly concentrated solutions are involved in the process in agreement with previous studies [30, 39, 58].

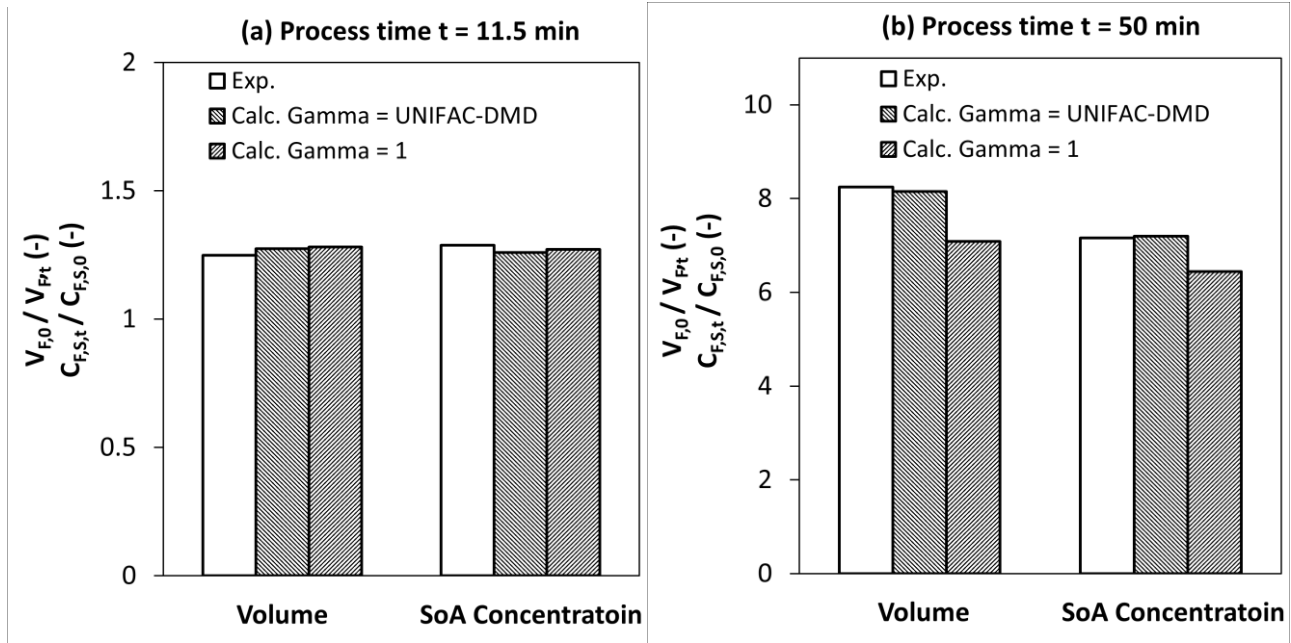


Figure 4.8: Experimental (exp.) and calculated (calc.) normalised volume and solute concentration during the batch concentration process of sucrose octaacetate in ethyl acetate with the 2.5"x40" spiral-wound membrane module and effect of thermodynamic non-ideality at different process times: (a) 11.5 minutes and (b) 50 minutes. The process was run at 30 °C and 30 bar with retentate flowrate of 300 L h⁻¹. Volume and solute concentration were normalised with respect to the initial solution volume ($V_{f,0}$) and solute concentration ($C_{f,s,0}$).

4.4 Conclusions

Experimental data on batch concentration process performance with three commercial SWMMs of different sizes up to 4.0"x40" in SoA / EA solutions under various pressures and retentate flowrates were reported. It was observed that increasing the feed pressure can accelerate the batch concentration process

and effectively reduce the solute loss to permeate due to the increase in both the permeate flux and rejection. Similarly, it was observed that increasing the retentate flowrate makes the concentration process slightly faster and decreases the solute loss to permeate. However, in an industrial application, increasing the feed pressure may damage the membrane when the feed pressure exceeds the maximum pressure the membranes can tolerate, and also brings more safety concerns. The increase of the retentate flowrate may cause telescoping and even damage the modules, and requires higher energy consumption. Therefore, during the process design, the optimal value of the feed pressure and retentate flowrate for a specific application has to be identified, in terms of process efficiency, solute recovery and energy consumption.

A mathematical model to describe the membrane batch concentration process was developed, based on combination of the classical solution diffusion membrane transport model and the film theory, to account for the mass transfer effects. The model was implemented using the “OSN Designer” software tool. The parameters of the membrane transport model were obtained from flat sheet test data and the parameters necessary to describe the pressure drops and the mass transfer characteristics of the modules were obtained from a regression procedure on a limited number of experimental data on the 1.8"X12" module under steady state conditions. The pressure drop through the permeate channel of the module was shown to affect significantly the performance of the batch concentration process, therefore it must be known, in order to accurately predict the performance of the batch concentration process using SWMMs. On the other hand, the effect of the feed pressure drop on the batch concentration performance was found to be negligible in this case study since the feed pressure drops were negligible (< 0.5 bar). However, the feed channel pressure drop may become important in industrial applications where several modules are connected in series. Besides, it was also found that the mass transfer resistance and thermodynamic non-ideality of the solution have to be taken into account, in order to accurately simulate the membrane batch concentration performance.

Very good agreement was found between the batch concentration performance data under various operating conditions and the simulation obtained by the multi-scale modelling procedure, indicating that the performance of a batch concentration process with a SWMM can be predicted from laboratory cross-flow flat sheet test data when both the fluid dynamics and mass transfer characteristics in the module and the necessary channel geometry are known. Moreover, the success of this approach in predicting the performance of the batch concentration process shows the potential for using this approach in other OSN processes, and the OSN Designer tool provides the possibility of obtaining the thermodynamic and physical properties of various solute/solvent combinations.

The process model presented in this chapter does not consider the effect of fouling on the process performance, since fouling was not observed from the module autopsy after the experiments, neither in a previous study featuring the same mock solutions and modules in Chapter 3. However, for a particular application where fouling is expected to affect the overall process performance, it is possible to modify the transport model in MATLAB code to include the occurrence of fouling (a suitable model to describe fouling should be identified for the specific application of the interest). Finally, this process model has the potential to do an optimisation since it can be used to simulate the process performance under various conditions and it has access to the build-in model analysis functions which can be applied to carry out process optimization and economic evaluation in Aspen Plus using the “OSN Designer”.

4.5 Acknowledgements

This chapter is reproduced from my own published paper (<http://dx.doi.org/10.1016/j.cherd.2016.02.005>). It is with permissions from ‘B. Shi, D. Peshev, P. Marchetti, S. Zhang, A.G. Livingston, Multi-scale modelling of OSN batch concentration with spiral-wound membrane modules using OSN Designer, Chem. Eng. Res. Des., 109, 385 – 396, Elsevier 2016’.

Chapter 5

Will ultra-high permeance membranes lead to ultra-efficient processes? Challenges for molecular separations in liquid systems

5.1 Introduction

The ultra-high membrane permeances reported in the literature are nearly always obtained from flat sheet membrane tests in either dead-end or cross-flow cells, and frequently employ pure solvents or highly dilute systems with solute concentrations $< 2 \text{ g L}^{-1}$. Under these conditions, pressure gradients across the membrane, osmotic pressure, and concentration polarisation are assumed to be negligible; and the reported permeances are the highest that can be obtained with the respective membrane. These are exclusively properties of the membrane and solvent, and they are referred to here as “intrinsic membrane permeance” values for that solvent. Industrial processes usually work at moderate concentrations, in the range 1 to 100 g L^{-1} (for example seawater desalination typically operates at NaCl concentrations between 30 and 70 g L^{-1}), and membrane modules rather than flat sheets are used in industrial processes. Nanofiltration and reverse osmosis achieve molecular separation when applied with appropriate membranes to organic solvent filtration or water treatment / desalination. While the physico-chemical properties of organic and aqueous solutions differ significantly, mass transfer and fluid dynamic limitations

are known to impact on both processes [10, 30, 39, 40, 110, 111]. The permeance in a system, defined as the ratio of flux to feed pressure, is referred to here as the “achieved system permeance”.

Previous studies [8 – 11] have reported that concentration polarisation is the main limitation on achieved system permeance for RO in SWMMs when high permeance membranes are utilized. They have recommended that high shear rates are used in the feed channels to improve mass transfer rates and reduce this limitation. These important studies teach that the overall system performance may not be controlled by the membrane itself, and lead to further avenues of enquiry. For example, in addition to limitations from concentration polarisation and pressure drop in feed channels, pressure drop in permeate channels is a further potentially important limitation on achieved system permeance, especially when high permeance membranes and high shear rates in feed channels are being utilised. These previous studies have not yet examined this factor, although there are indications that this may be significant in many cases (The details are shown in Chapter 3). Previous studies focus exclusively on RO. Since there is a growing body of literature on ultrahigh permeance membranes in OSN, it is of interest to examine the conditions under which concentration polarisation and/or pressure drop in the feed and permeate channels become significant limitations on achieved system permeance in OSN. Further, most of the previous studies on concentration polarisation and pressure drop focused on SWMMs, as they are the most commonly used for RO. As the permeate pressure drop in SWMMs becomes more important, it is useful to consider operating with hollow fibres which do not have permeate spacers. These might provide a more suitable platform for high permeance membranes

In this chapter, OSN and RO are used as case studies to probe the benefits of ultra-high permeance membranes. Firstly studies of ultra-high permeance membranes to ascertain the range of reported solvent permeances and the systems used to obtain these data are reviewed. Next the performance of flat sheet membranes in cross-flow cells is simulated, to evaluate the effect of increasing intrinsic membrane

permeance on achieved system permeance, under conditions where concentration polarisation occurs. In cross-flow cells, the pressure gradients are negligible due to the small size of the cells. Then the achieved system permeance as a function of the intrinsic membrane permeance for SWMMs, which are the most popular membrane modules for RO and NF, is simulated. In turn both pure solvent systems, in which pressure drops arise in the absence of concentration polarisation, and solute / solvent mixtures, in which both pressure drops and concentration polarisation can be significant are considered. Subsequently, simulations of an OSN batch concentration process and a continuous RO desalination process, both using SWMMs, are performed. These investigate whether ultra-high permeance membranes can make a significant impact on process efficiency with existing SWMMs. Research into overcoming the limitations on achieved system permeance imposed by concentration polarisation and pressure drop is summarised and compared in terms of technological characteristics and energy requirements. The advantages and limitations of other membrane module designs are also discussed, with special emphasis on the popular hollow fibre configuration, which offers the highest packing density among membrane modules.

5.2 Ultra-high permeance membranes for OSN and RO

5.2.1 Ultra-high permeance membranes for OSN

Polymeric membranes are highly interesting materials for OSN applications due to their relatively low price with respect to ceramic alternatives, and ease of fabrication and upscaling. Their potential in industrial concentration and purification processes has been demonstrated [13 – 15]. In order to improve the membrane performance and speed up the separation processes, considerable efforts have been made to enhance OSN membrane permeance without sacrificing selectivity. Key achievements in this area to date include those summarised in Table 5.1. They have been classified into five groups based on the approach the authors used to increase the membrane permeance: (1) fabrication of thin film composite membranes using high flux materials for the selective layer; (2) “activation” of membranes before filtration; (3) fabrication of membranes by adding nanomaterials into the membrane selective layer; (4) fabrication of

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membranes using blended polymers (5) fabrication of ultrathin membrane selective layers in the nanometer range.

Table 5.1: Summary of high permeance membranes for RO and NF in organic solvents. Five approaches were adopted: (1) fabrication of thin film composite (TFC) membranes using high flux materials for the selective layer (entries 1 – 3); (2) “activation” of membranes before filtration (entries 4 – 5); (3) fabrication of membranes by adding nanomaterials to the membrane selective layer (entries 6 – 12); (4) fabrication of membranes using blended polymers (entry 13) and (5) fabrication of ultrathin membrane selective layers in the nanometer range (entries 14 – 16). When more than one membrane, one solvent, one solute or one set of operating conditions were tested in the reference, the values corresponding to the highest permeance with a solute rejection near 90% or higher were taken

Entry	Membrane type and materials	Testing equipment	Filtration Temperature (°C)	Feed Pressure (Bar)	Testing solution	Solute concentration (mg L ⁻¹)	Permeance (L m ⁻² h ⁻¹ bar ⁻¹)	Solute rejection (%)	Ref.
1	TFC via IP, PPy / PAN	Dead-end cells	Room T	4	Rose Bengal (1017 Da) in tetrahydrofuran	71	67.1	98.0	[116]
2	TFC via casting, PTMSP / PAN	Dead-end cells	23	5	Remazol Brilliant Blue R (626.5 Da) in acetone	15	17.2	85.0	[117]
3	TFC via dip coating, PIM / PAN	Dead-end cells	Room T	3 – 6	Hexaphenylbenzene (534.7 Da) in n-heptane	8	3 – 7	87 – 92	[118]
4	TFC via IP, PA / PI	Cross-flow cells	30	30	Polystyrene oligomers (236 – 2000 Da) in acetone		2.4	~ 95.0 @	[119]
	UF				Alkanes (142.3 – 366.7 Da) in	1000	2.7	~ 90.0 @	[119]

					tetrahydrofuran			366.7 Da	
					Polystyrene oligomers (236 – 2000	3.8	~ 91.0 @	[120]	
					1200 Da) in toluene			698 Da	
5	ISA, (STARMEM™ 228)	PI Dead-end cells	20	30	Pure methanol	0	15.0	-	[121]
6	TFN, MOF-PA / UF	PI Cross-flow cells	30	30	Polystyrene oligomers (236 – 1000	11.1	~ 92.5 @	[122]	
					998 Da) in acetone			236 Da	
7	TFN, NaCl-PE /	PAN Dead-end cells	Room T	20	Rose Bengal (1017 Da) in -	28.5	100.0	[123]	
					tetrahydrofuran				
8	TFN, TiO ₂ -PA /	PAN Dead-end cells	Room T	5	Crystal Violet (408 Da) in 7.9	25.0	95.0	[124]	
					methanol				
9	TFN, GO-PPy /	PAN Dead-end cells	18	5	Rose Bengal (1017 Da) in 39.6	15.3	98.5	[125]	
					methanol				
10	ISA, GNP-CA	Dead-end cells	Room T	5	Pure ethanol	0	~ 0.5	-	[126]
11	ISA, GNP-PI	Dead-end cells	Room T	5	Pure ethanol	0	2.38	-	[127]

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12	ISA, GNP-PDMS	Dead-end	Room T	25	Pure ethanol	0	0.05	-	[128]
		cells							
13	ISA, PPSU & PI	Dead-end	21	20	Pure methylacetate	0	~ 100.0	-	[129]
		cells							
14	TFC via spin coating, PIM / PAN	Dead-end	30	13	Hexaphenylbenzene (534.7 Da) in n-heptane	10	~ 18.0	~ 90.0	[130]
		cells							
15	Acetylene nanosheets / Alumina support	Dead-end	20	0.8	Pure hexane	0	478.6	-	[131]
		cells	20	0.8	Pure 1-butanol	0	34.8	-	[131]
			25	0.8	Protoporphyrin-IX (562.7 Da) in ethanol	28.1	61.3	100.0	[131]
16	PA nanofilms / Alumina support	Dead-end	30	10	Pure acetonitrile	0	112.0	-	[132]
		cells			6-hydroxy-2-naphthalenesulfonic acid sodium salt (246.2 Da) in methanol	20	52.2	98.5	[132]

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TFC membranes consisting of thin dense polymer layers on top of porous support membranes generally prepared from another type of polymer have achieved excellent combinations of high permeance and good selectivity (see entries 1 – 3 in Table 5.1). Some examples are the formation of polypyrrole (PPy) thin films via interfacial polymerisation (IP) onto hydrolysed polyacrylonitrile (PAN) support membranes [116] and the formation of thin poly[1-(trimethylsilyl)-1-propyne] (PTMSP) films with controlled thickness on PAN supports [117]. Polymers of intrinsic microporosity (PIMs) were also used to develop TFC membranes of PIM-1 and PIM copolymers on PAN supports [118].

The permeance of membranes was enhanced also by immersion into specific “activating” solvents before filtration (see entries 4 – 5 in Table 5.1). The permeance of polyamide (PA) films cast on crosslinked polyimide (PI) was significantly improved by immersion into DMF before filtration [119, 120], while, similarly, the permeance of commercial PA- and PI-based membranes was significantly improved using alcohols, toluene, water and their mixtures, as activating agents [120, 121].

The permeance of membranes can be improved through addition of nanomaterials into the selective layer (see entries 6 – 12 in Table 5.1). A range of 50 – 150 nm metal-organic framework (MOF) nanoparticles [ZIF-8, MIL-53(Al), NH₂-MIL-53(Al) and MIL 101(Cr)] added into PA thin films on crosslinked PI UF supports reported almost 3 times increased permeance in THF without any change in selectivity [122]. Other successful examples of mixed matrix membranes for improved solvent permeance are sodium chloride ions added into polyelectrolyte (PE) on PAN supports, using the layer-by-layer electrostatic self-assembly technique [123], co-polyamide thin films incorporating aminated and chlorinated titanium dioxide (TiO₂) nanoparticles on PI UF supports [124] and graphene oxide (GO) incorporated into the top layer of PPy TFC membranes [125]. Local heating by light irradiation during the separation process was also used to increase the permeance of a membrane incorporating gold nanoparticles [126 – 128].

Integrally skinned asymmetric membranes consisting of blended polymers (polyphenylsulfone (PPSU) / PI) yielded higher permeance, with respect to the membranes made of either pure PPSU or PI [129] (see entry 13 in Table 5.1). This was attributed to the co-continuous structure and the very high interface area between the two polymers. Besides, activation of the membranes using acetone and methyl ethyl ketone increased both the methanol permeance and the rejection of Sudan II.

As solvent permeance is usually inversely proportional to the thickness of the membrane selective layer, the formation of ultrathin selective layers was also attempted to improve the membrane permeance (see entries 14 – 16 in Table 5.1). Ultrathin PIM layers ranging from 35 nm to 35 μm prepared via spin coating on PAN or alumina supports [130], ultrathin diamond-like carbon nanosheets with thicknesses ranging from 10 to 40 nm [131], and free-standing PA nanofilms less than 10 nm in thickness via interfacial polymerisation on porous alumina or cross-linked PI UF membranes [132] are significant examples. Some of these films achieved a permeance of about 1–3 orders of magnitude greater than commercial membranes with similar MWCOs [132].

5.2.2 Ultra-high permeance membranes for RO

Potable water scarcity is a pervasive global problem [110, 133]. Desalination is an important technology to produce potable water and RO is a leading desalination technology, contributing to about global desalination 65 % capacity [134, 135]. It is clear that enhancing the productivity of RO desalination plants can alleviate potable water scarcity and ease water stress. In recent years significant research has been devoted to developing high permeance RO membranes to improve the process productivity. The achievements to date include those summarised in Table 5.2. They have been classified into five groups based on the approach the authors used to increase the membrane permeance: (1) fabrication of membrane selective layers using high-flux natural materials; (2) modification of membrane surface; (3) modification of membrane supports; (4) fabrication of membranes by adding nanomaterials into the

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membrane selective layer; (5) fabrication of ultrathin freestanding GO membrane films in the nanometer range.

Table 5.2: Summary of high water permeance membranes for NF and RO. Five approaches were adopted: (1) fabrication of membrane selective layers using high-flux natural materials (see entries 1 and 2); (2) modification of membrane surface (entries 3 – 6); (3) modification of membrane supports (entry 7); (4) fabrication of membranes by adding nanomaterials into the membrane selective layer (entries 8 – 22); (5) fabrication of ultrathin freestanding GO membrane films in the nanometer range (entry 23). When more than one permeance and rejection data were reported, the values corresponding to the highest permeance with a salt rejection greater than 95 % were taken

Entry	Membrane type and materials	Testing equipment	Filtration Temperature (°C)	Feed Pressure (Bar)	Testing solution	Solute concentration (g L ⁻¹)	Permeance (L m ⁻² h ⁻¹ bar ⁻¹)	Solute rejection (%)	Ref.
1	Aquaporin-based / PSf	Cross-flow cells	20	10	Saline solution	~ 0.58	4.00	97.0	[136]
2	Aquaporin-based / PES	Cross-flow set-up	23	5	Saline solution	0.5	8.00	97.5	[137]
3	TFC, DMAEMA-PA	Cross-flow cells	25	15	Saline solution	~ 2	5.72	98.0	[138]
4	TFC, CBMA-PA	Cross-flow cells	25	15	Saline solution	~ 2	5.77	97.9	[138]
5	TFC, PVA-PA	Cross-flow cells	25	5	Saline solution	0.5	6.16	98.5	[139]
6	TFC, chitosan-PA / PSf	Cross-flow cells	19	8	Saline solution	~ 0.5	7.88	95.7	[140]

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7	TFC, PA / PSf-SiO ₂	Cross-flow cells	25	15.5	Saline solution	~ 2	3.55	99.1	[141]
8	TFC, <i>o</i> -ABA-TEA salt-PA / PSf	Cross-flow cells	25	15.5	Saline solution	~ 2	5.77	98.8	[142]
9	TFC, crosslinked PEG- <i>o</i> -ABA-TEA salt-PA / PSf	Cross-flow cells	25	15.5	Saline solution	~ 2	6.63	98.4	[143]
10	TFC, <i>o</i> -ABA-TEA salt-PA / PSf	Cross-flow cells	25	55.2	Saline solution	~ 32.8	1.37	99.4	[144]
11	TFC, AEPPS-PA / PSf	Cross-flow cells	25	15	Saline solution	~ 2	3.63	>98	[145]
12	TFC, GO-PA / PSf	Cross-flow cells	25	15.5	Saline solution	~ 2	1.06	99.4	[146]
13	TFN, GO-TiO ₂ -PA / PSf	Cross-flow cells	N/A	15	Saline solution	~ 2	3.42	99.5	[147]
14	TFN, GO-PAES	Dead-end cells	20	4	Direct Red 16 solution	16 3	13.25	96.0	[148]
15	TFN, aGO-GO-aPAES / PSf	Cross-flow cells	Room T	55	Saline solution	32	0.51	98.0	[149]
16	TFN, aGO-GO-PA / PSf	Cross-flow cells	Room T	15.5	Saline solution	2	0.90	96.4	[150]

	PSf								
17	TFN, GO-PA / PSf	Cross-flow cells	Room T	27.6	Saline solution	~2.9	1.50	97.8	[151]
18	TFN, ZIF-8-PA / PSf	Cross-flow cells	23	15.5	Saline solution	~ 2	3.35	98.5	[152]
19	TFN, NaY zeolite-PA / PSf	Cross-flow cells	25	15.5	Saline solution	~ 2	5.54	98.4	[153]
20	TFN, silicalite-1 nanozeolite-PA / PSf	Cross-flow cells	25	16	Saline solution	~ 2	4.16	96.4	[154]
21	TFN, carbon nanotube-PA / PES	n/a	n/a	13.8	Saline solution	~ 2	3.57	99.3	[155]
22	TFN, carbon nanotube-PA / PSf	Cross-flow cells	25	15.5	Saline solution	~ 3.75	3.31	98.5	[156]
23	Freestanding TiO ₂ films	GO- Vacuum filtration	n/a	1	Methyl orange solution	~ 0.01	7.00	100	[157]

Fabrication of membrane selective layers using high flux natural materials can achieve high permeance without sacrificing selectivity (see entries 1 and 2 in Table 2). Some examples are the formation of Aquaporin-based selective layers on polysulfone (PSf) flat-sheet substrate [136] and polyethersulfone (PES) hollow fibre substrate [137]. Hydrophilization is critical for improving the performance of reverse osmosis membranes in desalination, specifically for enhancing the membrane flux and improving anti-fouling properties [138]. Some studies showed that the membrane hydrophilicity can be changed by modifying the membrane surface (see entries 3 – 6 in Table 5.2). This was achieved by grafting zwitterionic carboxybetaine methacrylate polymer chains on the membrane surface [138], via covalent attachment of polyvinyl alcohol [139] or by supramolecular assembly of chitosan [140]. Other ways to increase the membrane permeance are modification of the support to improve support surface porosity (see entry 7 in Table 5.2) [141], or adding nanomaterials into membrane selective layers to change the membrane morphology (see entries 8 – 22 in Table 5.2). For the latter case, hydrophilic additives were added into PA RO membranes [142 – 147, 150 – 156] and poly(arylene ether sulfone) (PAES) membranes [148, 149], or cross-linked polyethylene glycol layers were coated on the membrane surface [153]. In addition, graphene, a 2-D layer of carbon atoms joined together in a hexagonal honeycomb matrix, and its derivatives such as GO and aminated GO (aGO) have great potential to advance the membrane desalination [158]. An example of ultrathin freestanding GO films were successfully tested at laboratory scale (see entry 23 in Table 5.2) [157].

Finally other studies have described theoretical results without experimental validation [159, 160]. These have indicated that water permeance can reach several orders of magnitude higher than conventional reverse osmosis membranes if single layers of graphene can be engineered to provide RO effective pores.

5.2.3 Summary

This brief review of relevant literature shows that membrane permeance has been increased into the range $20 - 100 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for OSN and about $5 - 13 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for RO. However, all these high permeances

reported in the literature in both OSN and RO were obtained from flat sheet membrane tests in either dead-end or cross-flow cells in pure or dilute solutions ($< 2 \text{ g L}^{-1}$). Looking ahead based on this excellent progress, it seems reasonable to assume that further advances will continue and that membranes with permeances over $100 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for OSN and over $13 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for RO will eventually be reported. This raises two important questions: (1) what will be the benefits of these membranes in the moderately concentrated systems typical of real world applications? and (2) are current module designs available to exploit these advances?

5.3. Limitations on Achieved System Permeance – concentration polarisation and pressure gradients

5.3.1 Effect of concentration polarisation on achieved system permeance for flat sheet membranes

It is generally expected that the membrane flux will increase with increasing applied pressure, or with increasing membrane permeance. However in systems with retained solutes, according to the film theory, concentration polarisation becomes stronger as flux increases [10, 39, 112]. To examine the impact of concentration polarisation, the performance of flat sheet membranes in cross-flow cells is simulated below. In these systems the mass transfer coefficient is usually in the order of $10^{-5} - 10^{-4} \text{ m s}^{-1}$ in both OSN and RO applications [39, 161, 162], and in this chapter the mass transfer coefficients are in this range. A mathematical model combining the classical solution-diffusion model for membrane permeation and the film theory for boundary layer mass transfer has been utilised. Gradients of concentration, pressure and velocity in the cells were ignored due to their short flow path. Solute/solvent systems including solutions of sucrose octaacetate / ethyl acetate and NaCl / water were chosen as model solutions for OSN and RO, respectively, due to the availability of their thermodynamic and physical properties in the literature [163] and in the previous chapters (Chapters 3 and 4).

Figure 5.1(a) explores how the achieved system permeance (ASP) changes with mass transfer coefficient in a 10 wt% solution of SoA/EA. It is shown that when the mass transfer coefficient is infinitely large (i.e. negligible solute accumulation at the membrane surface), the ASP in the solute/solvent system increases linearly with intrinsic membrane permeance (solid line). Under these ideal conditions concentration polarisation does not occur. It is worth noting that, even when no concentration polarisation occurs, the ASP is still lower than in pure solvent, due to the osmotic pressure exerted by the solute. When the mass transfer coefficient is between 10^{-5} and 10^{-4} m s^{-1} (dashed, dotted and dashed-dotted lines, respectively), concentration polarisation reduces the ASP so that as the intrinsic membrane permeance increases, a plateau is reached at a certain (critical) value. Once this plateau is reached, further increases in intrinsic membrane permeance will not increase the ASP, similar to results reported by McGovern and Lienhard V [112]. The lower the mass transfer coefficient, the smaller the critical intrinsic membrane permeance value and the lower the value of ASP at the plateau. The degree of concentration polarisation is also affected by the feed concentration. The higher the feed concentration, the more severe the occurrence of concentration polarisation, and in turn the lower the critical values of intrinsic membrane permeance at which the ASP plateau is reached (see Figure 5.1(b)). Figures 5.1(c) and 5.1(d) show that similar effects of mass transfer coefficients and feed concentration also occur for the RO example. In the RO system, the critical intrinsic membrane permeance value for pure water is much smaller than that for pure solvent under the same mass transfer and feed concentration conditions (compare both solid and dashed lines in Figures 5.1(b) and 5.1(d)), due to the higher osmotic pressure in the NaCl/water solutions compared to that in the SoA/EA solutions with the same weight solute concentration. This trend may change when different solutions are applied.

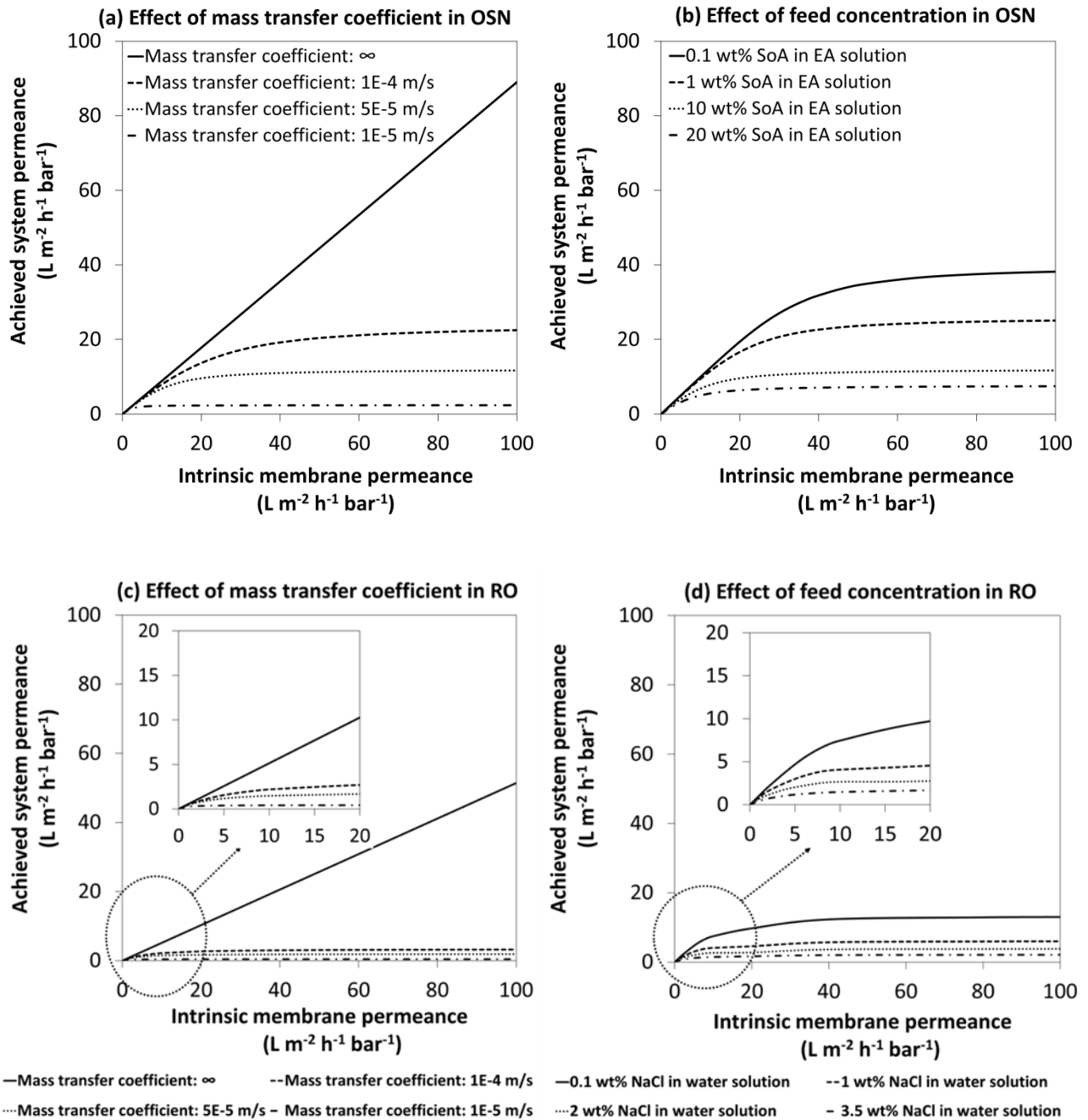


Figure 5.1: Simulations of achieved system permeance against intrinsic membrane permeance using cross flow cells under steady state operation: (a) effect of mass transfer coefficient for a 10 wt% SoA/EA solution; (b) effect of SoA concentration for a mass transfer coefficient of $5\text{E-}5 \text{ m s}^{-1}$; (c) effect of mass transfer coefficient for a 3.5 wt% NaCl/water solution; and (d) effect of NaCl concentration for a mass transfer coefficient of $5\text{E-}5 \text{ m s}^{-1}$. The system performance is simulated at 30°C and 30 bar for OSN and at 25°C and 55 bar for RO. The rejection of the solutes (SoA and NaCl) is assumed to be 100 %. Details of the simulation can be found elsewhere [39, 163 – 166].

5.3.2 Effect of pressure drop on achieved system permeance in SWMMs

SWMMs are the most popular membrane module design applied in industry for NF and RO due to their good balance between high packing density, ease of operation, low fouling tendency and low cost. In a SWMM, the feed fluid is forced to flow longitudinally through the feed channel, usually across feed spacers that both hold the membrane leaves apart and promote turbulence and mass transfer; while the permeate flows inwards to the central collection tube through the permeate spacer, which resists the applied pressure forcing the membranes together. Both of these flows incur pressure drops through these channels, and in this section, the effect of these pressure drops on the achieved system permeance, in the absence of concentration polarisation, is investigated. This is undertaken via simulation of a 2.5"x40" module for OSN and an 8.0"x40" module for RO, respectively, considering variable intrinsic membrane permeance and pure solvent/water.

As can be seen in Figure 5.2, in both organic solvent and water, the achieved system permeance (dashed line) increases with the intrinsic membrane permeance at values, then tends towards a plateau at higher permeance values. This is because at higher intrinsic membrane permeance the volume of fluid permeating through the membrane increases, in turn increasing the linear velocity through the permeate spacer and raising the pressure drop in the permeate side, as explained in Chapter 3. This significantly reduces the effective driving force, i.e. the transmembrane pressure difference. When the intrinsic membrane permeance increases beyond a critical value, the permeate pressure drop becomes limiting and the achieved system permeance reaches a plateau after which further increasing the intrinsic membrane permeance has no further effect on the overall module permeance. The effect of the feed pressure drop on the module performance is less significant than the effect of the permeate pressure drop (see Chapter 3), however it may become significant when several modules are connected in series in industrial applications. It is noticeable by comparing Figures 5.2(a) and 5.2(b) that the critical membrane permeance in OSN is smaller than that in RO, indicating that the permeate pressure drop in OSN is more severe. This is because the permeate spacer in the OSN module has different geometry with that in the RO module (EMET-P1 (see

Chapter 3 for details) vs. FilmTec FT30 [88]), resulting in different friction coefficient correlations (see Chapter 3 and [88] for details). The effect of concentration polarisation on SWMM performance in RO has been documented by others [112 – 115], and building on these studies this work shows that in addition the permeate pressure drop is likely to become a very significant consideration as the intrinsic membrane permeance increases. The large gap between the ideal module (no pressure drop effect, solid line) and the real module (dashed line) shows that there is still potential for improvement from the module design point of view. One obvious change would be to make the permeate spacer thicker, and so present a higher cross sectional area for the permeate flow. However, thicker permeate spacers mean that less membrane area can be fitted into a given module diameter; and one can foresee that as intrinsic membrane permeance increases, there will be an optimum permeate spacer thickness to obtain the maximum permeate flow from a module. The point made here remains valid however: for a SWMM, increasing intrinsic membrane permeance will not automatically produce increases in achieved system permeance, due to the steep pressure gradients produced when employing ultra-high permeance membranes.

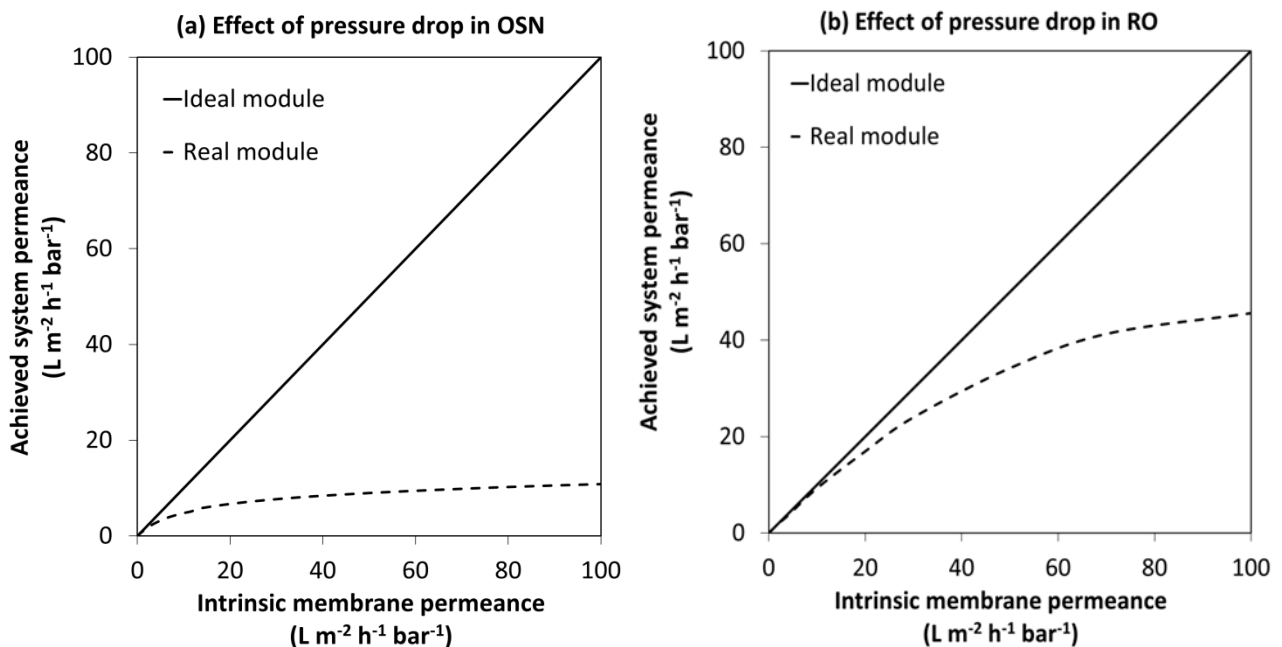


Figure 5.2: Achieved system permeance in SWMM as a function of the intrinsic membrane permeance for pure solvents under steady state operation: (a) in pure EA at 30 °C and 30 bar; (b) in pure water at 25 °C

and 55 bar. The retentate flowrate was fixed at 1000 L h^{-1} and 7500 L h^{-1} for a 2.5"x40" OSN SWMM and a 8.0"x40" RO module, respectively. The simulation was carried out using the model reported in Chapter 3 for OSN and [88, 163, 165 – 168] for RO.

5.3.3 Effects of combined concentration polarisation and pressure drop on achieved system permeance in SWMMs

In a real process featuring membrane modules, the effects of concentration polarisation and pressure drop co-exist and influence each other. Figure 5.3 considers the same solute/solvent systems as the flat sheet membranes of Figure 5.1, but with the membranes now in SWMMs as described above for Figure 5.2. Comparing Figure 5.3 with Figure 5.2, it can be seen that the increase in the achieved system permeance as intrinsic membrane permeance increases, for both EA and water, is reduced by the concentration polarisation and osmotic pressure. These more severe limitations result in significantly lower critical values of intrinsic membrane permeance for both SoA/EA and NaCl/water systems. It is worth noting by comparing the same figures that the achieved permeance of the ideal module in solution (no concentration polarisation, no pressure drop, no gradients of concentration) is also worse than the membrane permeance in pure solvent / water, due to the effect of the osmotic pressure. The overall conclusion from this analysis is that increases in intrinsic membrane permeance from materials science advances will be difficult to transfer into the SWMMs that will be used in practise.

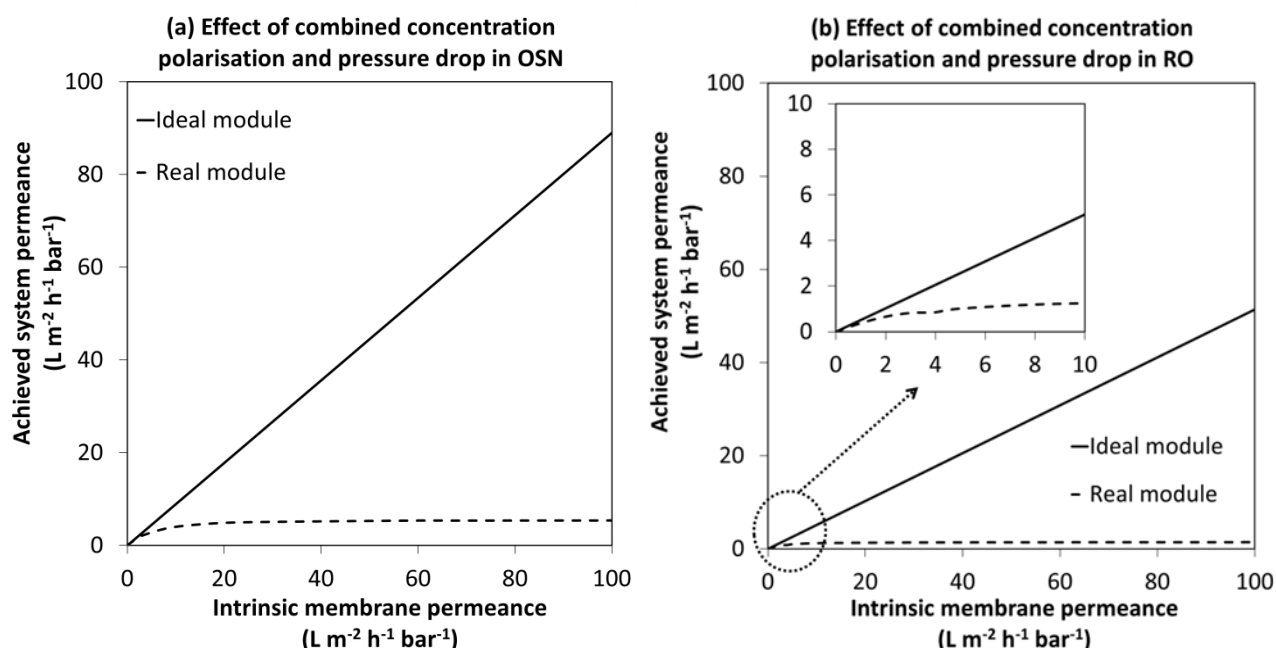


Figure 5.3: Profile of the achieved system permeance in SWMMs in solute/solvent systems versus the intrinsic membrane permeance under steady state operation: (a) in 10 wt% SoA/EA at 30 °C and 30 bar; (b) in 3.5 wt% NaCl/water at 25 °C and 55 bar. Solute rejection (SoA and NaCl) is assumed to be 100%. The retentate flowrate was fixed at 1000 L h^{-1} and 7500 L h^{-1} for a 2.5"x40" OSN SWMM and a 8.0"x40" RO module, respectively. The simulation was carried out using the model reported in Chapter 3 for OSN and [88, 163, 165 – 168] for RO.

5.3.4 Will ultra-high permeance membranes lead to more efficient processes?

The consequences of concentration polarisation and pressure drop are significant not only at the module scale (module flux and solute rejection) but also at the process scale, in terms of productivity and operating time. A key motivator for research on high-permeance membranes is to bring about more efficient processes, able to filter large volumes of solvents or water in a short operating time. In light of the above, is this really possible with the current technology at the disposal?

To investigate whether ultra-high permeance membranes can lead to fast processes, two case studies are analysed: (a) an OSN batch process to concentrate 80 L of SoA / EA solution from 10 wt% to 40 wt% using a

single 2.5"x40" SWMM; and (b) a continuous RO desalination process using a single 8.0" x40" SWMM. Figure 5.4 shows results from these simulations. In Figure 5.4(a) increasing intrinsic membrane permeance significantly accelerates the process when the membrane permeance is $< 10 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. After this, further increases in intrinsic permeance do not speed up the batch concentration since the achieved system permeance becomes limited by concentration polarisation and pressure drop. In the RO desalination process, increasing the intrinsic membrane permeance also introduces negligible benefit for the process productivity when the membrane permeance is $> \sim 5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, due to the limitations of the concentration polarisation and pressure drop in the modules (see Figure 5.4(b)). A similar limitation introduced by concentration polarisation and pressure drop was also observed in RO and forward osmosis desalination [165]. Under these conditions, fluid dynamic and mass transfer are therefore obstacles that reduce or nullify the benefits of any improvement in the intrinsic membrane permeance.

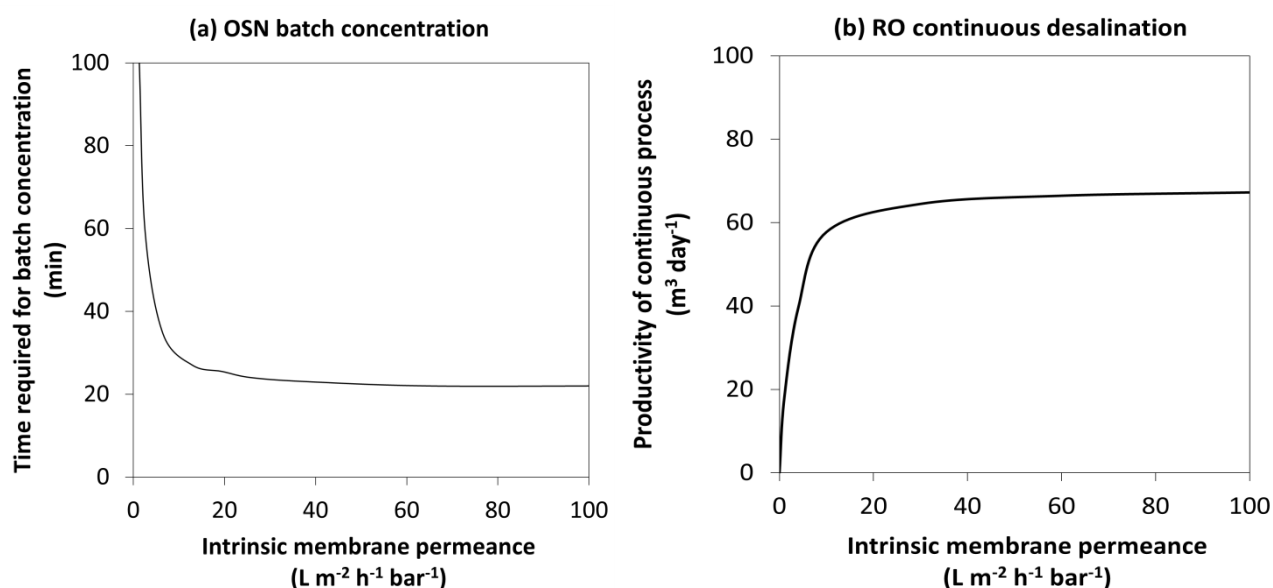


Figure 5.4: Effect of intrinsic membrane permeance on process efficiency using SWMMs: (a) time required for an OSN batch process to concentrate 80 L of SoA/EA solution from 10 wt% to 40 wt% at 30 °C and 30 bar; (b) productivity of a RO continuous desalination process at 25 °C and 55 bar. Solute rejection (SoA and NaCl) is assumed to be 100 %. The retentate flowrate was fixed at 1000 L h^{-1} and 7500 L h^{-1} for a 2.5"x40"

OSN SWMM and a 8.0"x40" RO module, respectively. The simulation was carried out using the model reported in Chapter 4 for OSN and [88, 161, 163, 164, 168] for RO.

5.3.5 Improvements in SWMM design

Because pressure gradients and concentration polarisation create limitations in SWMMs, design improvements have received attention. Three main approaches have been taken: (1) optimisation of spacer geometry: specifically, feed spacers are sought to introduce high mass transfer with minimum pressure drop, and permeate spacers to provide sufficient mechanical support with minimum pressure drop; (2) shortening the permeate channel length via using more membrane leaves, or using thicker permeate spacers; (3) altering the operating conditions including increasing the feed flowrate to increase mass transfer rates. For the first approach, both experiment and simulation have been used to demonstrate how various spacers perform in aqueous solutions [10, 89 – 100]. It is illustrated here how the optimisation of the spacer might significantly improve module performance using two different feed spacers and two different permeate spacers (see Table 5.3 and Figure 5.5).

Table 5.3: Spacer geometry and correlations for the friction coefficient and Sherwood number in the spacer-filled channels. All the information is taken from [92, 88]

Spacer code	H (mm)	d _h (mm)	ε (-)	Friction coefficient correlation	Sherwood number correlation	Reference
F1	2.1	0.66	0.466	$f_F = 0.91 Re_F^{-0.23}$	$Sh_F = 0.0096 Re_F^{0.66} Sc_F^{0.58}$	[92]
F2	0.82	0.97	0.88	$f_F = 6.23 Re_F^{-0.3}$	$Sh_F = 0.065 Re_F^{0.875} Sc_F^{0.25}$	[88]
P1	0.24	0.11	0.59	$f_P = 13 Re_P^{-0.8}$	-	[88]
P2	0.325	0.23	0.73	$f_P = 105 Re_P^{-0.8}$	-	[88]

It can be seen from Figure 5.5 that the combination of feed spacer F2 and permeate spacer P1 gives the best overall performance. However, the critical membrane permeance of $< 5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ in the module with the spacer F2 indicates that current module design will still not be for high permeable membranes (up to about $5 - 13 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, currently achievable as flat sheet format; see Table 5.2). Besides, the effect of permeate spacer is not observed in this case since the permeate flow is low and does not create significant permeate pressure drop even when high permeance membranes are used. This effect would become significant if more advanced feed spacers were available.

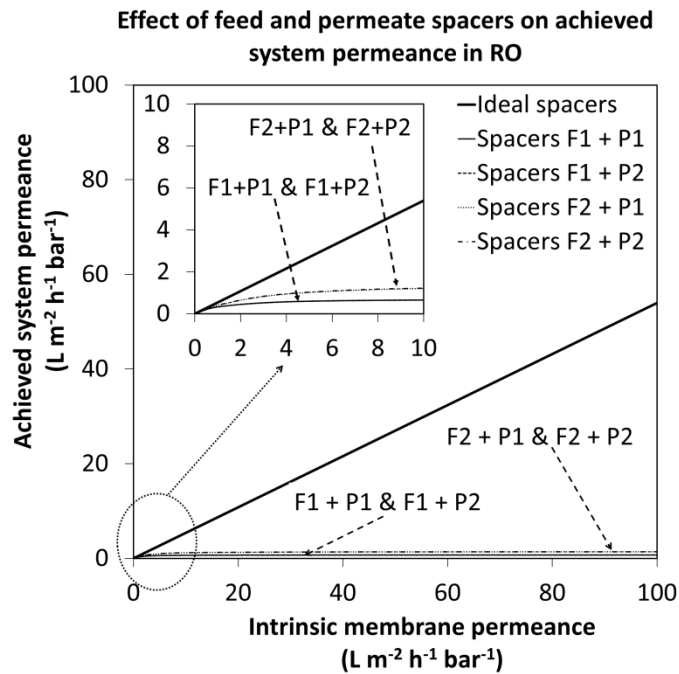


Figure 5.5: Effect of the feed and permeate spacers on the performance of the SWMM in 3.5 wt% NaCl/water solution at 25 °C and 55 bar under steady state operation. The retentate flowrate was fixed at 7500 L h^{-1} for a $8.0'' \times 40''$ RO module. Solute rejection (NaCl) is assumed to be 100 %. The effect of spacer geometry on module configuration is not accounted for. The simulation was carried out using the model reported in [88, 163, 165, 166, 168].

Increasing the retentate flowrate through modules is also an option to enhance the mass transfer and therefore decrease the extent of concentration polarisation. However, the consequence is an increase in both the specific energy consumption and feed pressure loss. The specific energy consumption, SEC, was calculated using Equation (5.1) [165].

$$SEC = \frac{F_f \cdot P_f}{F_p} \quad \text{Equation (5.1)}$$

F_f and F_p are the feed and permeate flowrate, respectively, and P_f is the feed pressure. As expected, increasing intrinsic membrane permeance significantly improves achieved system permeance (see Figure 5.6(a)) and reduces specific energy consumption (see Figure 5.6 (b)) when the membrane permeance is < 20 L m⁻² h⁻¹ bar⁻¹. After this, further increases in intrinsic permeance do not have obvious benefits. Furthermore, increasing retentate flowrate can increase achieved system permeance especially when the intrinsic membrane permeance is high (the concentration polarisation is severe), but consumes more energy. For example, at a membrane intrinsic permeance of 26 L m⁻² h⁻¹ bar⁻¹, an increase in the achieved system permeance of around 20 % results from increasing the retentate flowrate by about 500 % (see Figure 5.6(a)). The penalty is that the specific energy consumption increases by about 226 % (see Figure 5.6(b)). It is notable that there is a large gap between the real and ideal performance (see Figure 5.6(a)), and simple increasing the retentate flowrate is insufficient for improving module performance. In addition, the enhancement of the retentate flowrate causes a 10-fold increase of the feed pressure drop (up to about 2.5 bar), thus increasing the risk of telescoping, and damage to the module (see Figure 5.6(c)). Similar observations regarding the effects of retentate flowrate on module performance and specific energy consumption are found for RO desalination [165].

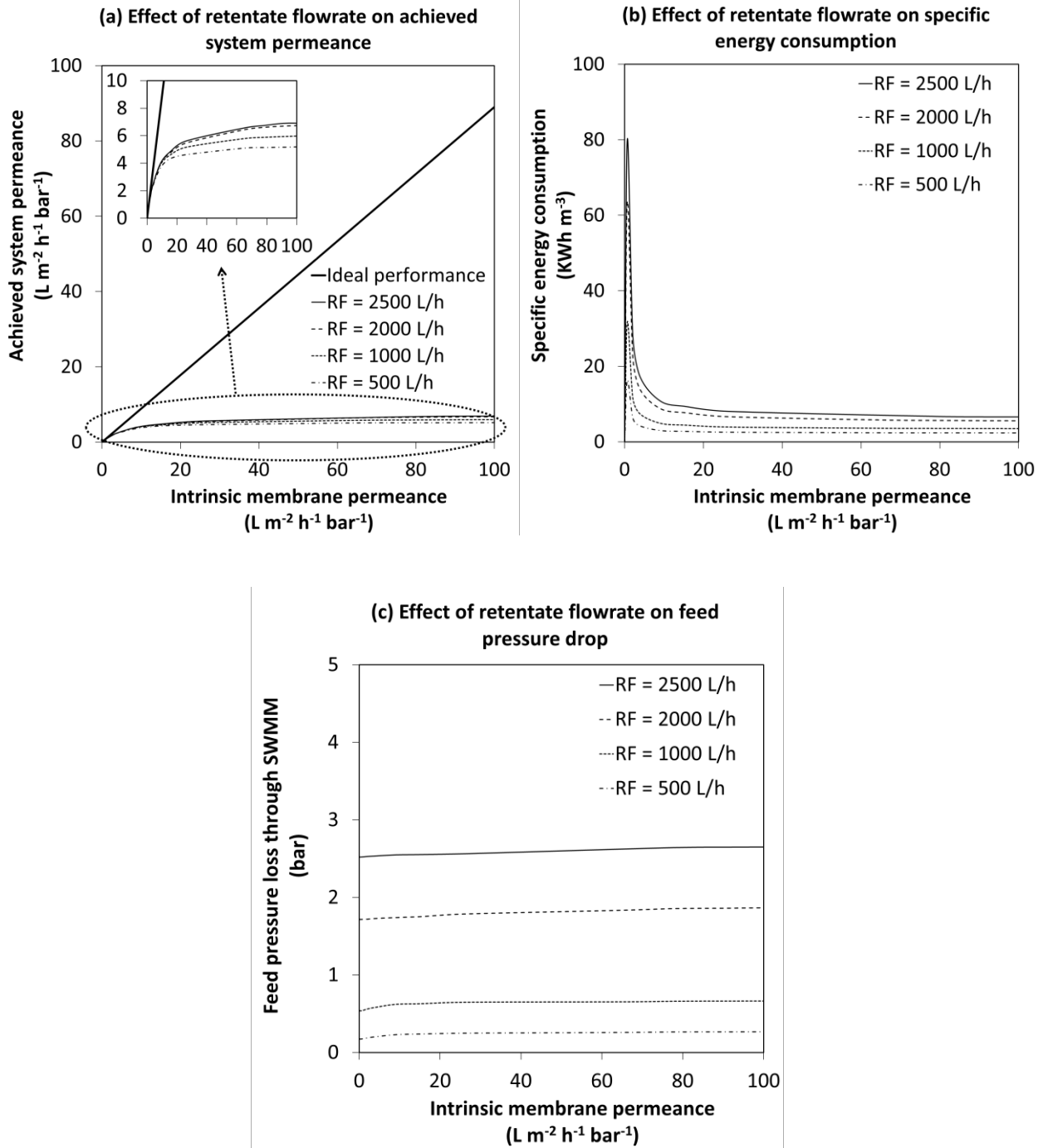


Figure 5.6: Effect of the retentate flowrate (RF) on the performance of the SWMM in 10 wt% SoA/EA solution at 30 °C and 30 bar under steady state operation. (a) achieved system permeance; (b) specific energy consumption; (c) feed pressure drop through the SWMM. Solute rejection (SoA) is assumed to be 100 %. The simulation was carried out using the model reported in Chapter 3.

5.4 Alternatives to spiral-wound membrane modules

Alongside the commonly used SWMMs, other membrane module designs are used in industrial applications, such as the plate-and-frame, tubular, capillary and hollow fibre configurations. Plate-and-frame modules are made of flat sheet membranes, supporting spacers, layered in the permeate channels between the membranes. They have a simple and robust structure, however, their low packing density and time-consuming installation have limited their applications in industry. Tubular membrane modules are configured in cylindrical multichannel prototypes or hollow fibre configurations. Compared to SWMMs, multichannel tubular modules have lower packing density and, therefore their applications in industry are relatively scarce.

Hollow fibre membrane modules consist of a bundle of fibres contained in a pressurised vessel. They can be fabricated in two geometries, shell-side feed design and bore-side feed design. The greatest advantage of HFMMs is that they can pack a very large membrane area into a single module. They also do not require feed or permeate side spacers, and have low permeate pressure drops. Given the issues identified above with SWMMs, particularly that the permeate side pressure drop creates severe limitations on achieved system permeance as the intrinsic membrane permeance increases, it is considered below whether HFMM's might provide a better platform for taking advantage of ultra-high permeance membranes.

Figure 5.7 shows the simulation of the performance of an RO continuous desalination process using a HFMM in a shell-side operation mode under different membrane conditions. Feed water is provided to the outside of the hollow fibres and permeate recovered from the inside channels. When the intrinsic membrane permeance for pure water is lower than $\sim 0.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, increasing the membrane permeance can significantly improve the process productivity; however, further increasing the membrane permeance beyond $0.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ shows negligible benefits for the process productivity due to, again, the limitations of concentration polarisation and pressure drop in the HFMM.

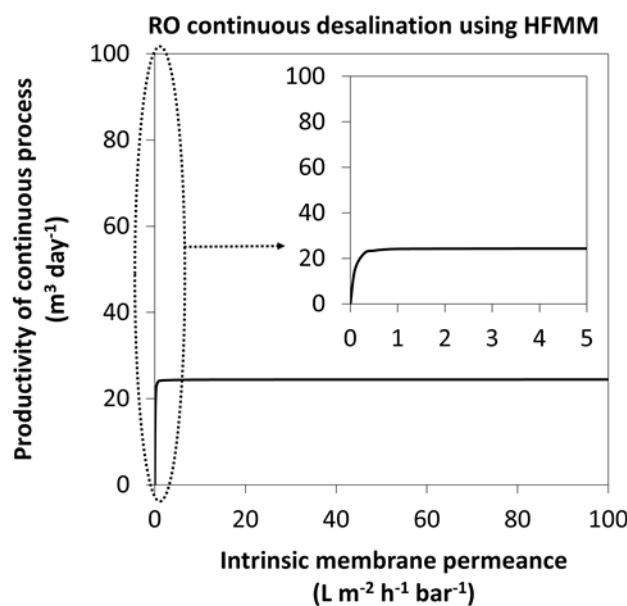


Figure 5.7: Effect of intrinsic membrane permeance on productivity of an RO continuous desalination process using a HFMM at 25 °C and 55 bar. Solute rejection (NaCl) is assumed to be 100 %. The feed bulk velocity is fixed at 0.01 m s^{-1} . The details of the simulation and the HFMM configuration are available in [163, 167 – 170].

The non-uniform fibre spacing in HFMMs has been reported to result in a flow mal-distribution and a reduction of the average mass transfer coefficient [171]. To overcome this problem, several researchers have introduced either (i) fibre-woven fabric into HFMMs to gain more uniform spacing; or (ii) baffles to create better mixing [170]. Some authors developed hollow fibres with wave-like geometries such as crimped, braided and twisted, to make the flow distribution even and enhance the mass transfer coefficient [172 – 174]. However, these techniques were not powerful enough to significantly enhance the mass transfer coefficient for high permeance membranes [170]. Another approach to enhance mass transfer is active enhancement techniques such as bubbling systems [175], vibrating membranes [176, 177] and ultrasonic systems [178, 179]. Although it has been shown that these active techniques can reduce concentration polarisation, it is also fair to comment that they consume significantly more energy, thus losing to some extent one of the advantages of using membranes for processing [170]. As an example, in the treatment of diluted skim milk using vibratory shear-enhanced process, in order to increase the

permeate flux by about 3 times and reduce the chemical oxygen demand in the permeate water about 5 times, the specific energy demand was almost doubled [180, 181].

Some novel membrane module designs which can reduce concentration polarisation and pressure drop effects have been investigated. Good examples include an envelope-type membrane module developed by GMT, which introduces less permeate pressure drop due to its short permeate channels [13]; furthermore, rotating membrane disks with vibrations were proposed to enhance the mass transfer and thus significantly eliminate the occurrence of concentration polarisation [182]. However, these novel designs have their own limitations: the envelope-type membrane module has lower membrane packing density and mechanical strength, compared to SWMMs or HFMMs, and rotating disks with vibrations consume a large amount of energy to create the vibrations. Nevertheless they may become more widely applicable if ultra-high permeance membranes are to reach the market.

5.5 Conclusions

A growing number of reports describing membranes with ultra-high permeance are appearing, with the aim of eventually making industrial processes more efficient. The paradigm supporting this search for higher permeance teaches that ultra-high permeance will lead to a reduction in process time for a given membrane area, or a major reduction in membrane area for a specific task. This paradigm is examined by considering the intrinsic membrane permeance as an independent variable in a range of simulations. In these simulations concentration polarisation and pressure drops in both feed and permeate channels, in membrane modules, are taken into consideration, in calculating achieved system permeance as function of the intrinsic membrane permeance. The main conclusion is that these two phenomena will become severely limiting above values of $10 - 20 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ in OSN, and $3 - 5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ in RO. These are values well within the range of reported membranes – and so even higher permeances are likely to have

little impact unless there is a parallel increase in the performance of membrane modules which improves mass transfer and reduces permeate side pressure losses.

Further, membrane modules have three important performance aspects. The first is the permeance they can achieve; the second is their selectivity, or ability to discriminate between molecules (particularly important for organic systems); and the third is their operational stability over time. In this latter aspect both the propensity of a module to undergo physical aging, and the propensity for fouling in the module are considered. The conclusion from this study is that further research on ultra-fast permeance might not have a significant practical impact on membrane processes. Rather, it might be worth considering to direct membrane research away from the search for ultra-high permeance in favour of prioritizing three related areas (i) membrane module design; (ii) improving nanofiltration selectivity; and (iii) reducing physical aging and fouling in modules.

5.6 Acknowledgements

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Chapter 6

Conclusions and future perspectives

The deep understanding of the impacts of SWMMs on the OSN processes and a reliable process model, which can account for the molecular transport through membranes, the fluid dynamics and mass transfer characteristics in the SWMMs, and the thermodynamic and physical properties of solution of interest as a function of operating conditions, positively contribute to the transfer of the OSN technology from R&D to real industrial applications. Below, the conclusions from this research are summarised, and some future perspectives in the field are outlined.

Chapter 3 Performance of SWMMs in OSN – fluid dynamics and mass transfer characteristics

Experimental data for the performance of four SWMMs provided by a membrane module manufacturer (EMET) was reported, in 0 – 20 wt% solutions of SoA in EA under various pressures and retentate flowrates in a steady-state mode. These modules were made with two different types of membranes (a commercial membrane, PuraMem® S600, and a development product, Lab-1, from EMET) and covered three standard module sizes (1.8"x12", 2.5"x40" and 4.0"x40"). All modules had the same commercial feed and permeate spacers. It was observed that the permeance and the rejection of the target solute in the module was always slightly lower than the same membranes in flat sheet configuration especially when the solution concentration was high and the retentate flowrate was low. In addition, the modules made of the same membranes but with different sizes also had different performance especially with respect to the

permeance. All these differences can be explained by the occurrence of concentration polarisation and pressure drop in the modules, strongly affected by different module configurations.

A procedure was developed to obtain the correlations for describing the Sherwood number and friction coefficient in any SWMM of interest using a few experimental data for flat sheets and one 1.8"x12" module, without the need to know spacer geometry a priori. This procedure was then verified in the applications of the four SWMMs in SoA/EA solutions. Three regression procedures were used here: (1) the unknown parameters in the selected membrane transport model (classical SD model) were obtained from regression of experimental flat sheet data (both PuraMem® S600 and Lab-1); (2) a correlation to characterise the friction coefficient in the feed channel together with the parameters describing the geometry of the feed channel, was determined by regression of the feed pressure drop data through the 1.8"x12" module; (3) a correlation for the friction coefficient in the permeate channel and a correlation for the Sherwood number in the feed channel were determined by regression of the module performance data in the solutions, using the classical SD model combined with the film theory. The parameters describing the geometry of the permeate channel were also obtained in the same regression procedure. It is then demonstrated that the obtained correlations and parameters can be extended to describe the fluid dynamics and mass transfer characteristics in the other modules, which have larger sizes and/or are made of different membranes but with the same feed and permeate spacers, via the successful simulation of the module performance in the solutions.

Chapter 4 Multi-scale modelling of OSN batch concentration with SWMMs using OSN Designer

Experimental data for the performance of batch concentration processes with three SWMMs made of commercial PuraMem® S600 membranes and of different sizes up to 4.0"x40" were obtained, in SoA/EA solutions under various pressures and retentate flowrates. It was observed that increasing the feed pressure can accelerate the batch concentration process and effectively reduce the solute loss to permeate

due to the increase in both the permeate flux and rejection. Similarly, it was observed that increasing the retentate flowrate makes the concentration process slightly faster and decreases the solute loss to permeate. However, in an industrial application, increasing the feed pressure may damage the membrane when the feed pressure exceeds the maximum pressure the membranes can tolerate, and also brings more safety concerns. The increase of the retentate flowrate may cause telescoping and even damage the modules, and requires higher energy consumption. Therefore, during the process design, the optimal value of the feed pressure and retentate flowrate for a specific application has to be identified, in terms of process efficiency, solute recovery and energy consumption.

A multi-scale process model considering molecular transport through membranes (membrane scale), the fluid dynamics and mass transfer characteristics in SWMMs (module scale) and the thermodynamic and physical properties of the solution of interest as a function of operating conditions (process scale), was developed in the “OSN Designer” software tool. It was then used to simulate the performance of a batch process to concentrate SoA / EA solutions using different SWMMs under various pressures and retentate flowrates. The simulation results showed that the pressure drop through the permeate channel of the module significantly affects the performance of the batch concentration process. The effect of the feed pressure drop on the batch concentration performance was found to be negligible in this case study since the feed pressure drops were negligible (< 0.5 bar). However, the feed channel pressure drop may become important in industrial applications where several modules are connected in series. Besides, it was also found that the mass transfer resistance and thermodynamic non-ideality of the solution have to be taken into account, in order to accurately simulate the membrane batch concentration performance. Very good agreement was found between the experiments and the simulation, indicating that the performance of a batch concentration process with a SWMM can be predicted from laboratory cross-flow flat sheet test data when both the fluid dynamics and mass transfer characteristics in the module and the necessary channel geometry are known (these parameters can be obtained using the procedure developed in Chapter 3). Moreover, the success of this approach in predicting the performance of the batch concentration process

shows the potential for using this approach in other OSN processes, and the “OSN Designer” tool provides the possibility of obtaining the thermodynamic and physical properties of various solute/solvent combinations of interest.

Chapter 5 Will ultra-high permeance membranes lead to ultra-efficient processes? Challenges for molecular separations in liquid systems

The effect of intrinsic membrane permeance on achieved system permeance was studied via simulation in both the OSN and RO applications. It is found that the main limitation for the membrane/process performance will transition from the intrinsic membrane permeance to concentration polarisation and pressure drop limitations, when the intrinsic membrane permeance reaches a critical value. This means that further increasing the intrinsic membrane permeance beyond a critical value has no benefit on the process efficiency. This critical value depends on the module design and the operating conditions. Furthermore, efforts in module development were discussed in terms of technological characteristics and energy requirements. Shortening permeate channels by using thicker spacers and/or applying more membrane leaves can effectively reduce the pressure drop through the permeate channel. This is however at the cost of sacrificing membrane packing density, and in turn effective membrane area. Besides, from a manufacturing point of view, shortening permeate channels makes the module fabrication more complicated, almost impracticable for very short permeate channels. Increasing the mass transfer coefficient can reduce the occurrence of concentration polarisation. Practically this can be achieved by enhancing the retentate flowrate; however, this can cause larger feed pressure drop, thus increasing the risk of telescoping, and damage to the module. Furthermore, achieving higher retentate flowrate requires higher energy consumption. Optimising the feed and permeate spacer geometry to improve the local mass transfer and the fluid dynamics in the channels is another flexible way to overcome the limiting effects of concentration polarisation and pressure drop in the modules. Specifically, feed and permeate spacers should have the ability to enhance the mass transfer coefficient and provide enough mechanical support, respectively, while causing minimum pressure drop. However, the current spacer design is not optimal in

terms of mass transfer enhancement for ultra-high permeance membranes. Besides, alternative membrane module designs, such as the plate-and-frame, tubular, capillary and hollow fibre configurations, and some novel designs such as an envelope-type module and a rotating disc are commented on in terms of their advantages and disadvantages. As a conclusion, further research on ultra-fast permeance might not have a significant practical impact on membrane processes. Rather, it might be worth considering to direct membrane research away from the search for ultra-high permeance in favour of prioritizing three related areas (i) membrane module design; (ii) improving nanofiltration selectivity; and (iii) reducing physical aging and fouling in modules.

Overall, this research project has provided a major step forward in the understanding of the fluid dynamics and mass transfer characteristics in the SWMMs and their impacts and limitations in OSN applications. However, there are still many new avenues of research that require considerable work to fulfil OSN's ultimate potential:

- More experimental data are needed for the performance of SWMMs made of different commercial membranes in various applications of interest in different operation modes, such as steady-state mode, concentration batch model and diafiltration/purification process. Although this is comprehensively time consuming and expensive, it can to significant extent enhance the confidence of chemical industries on this novel technology, and accelerate its breakthrough.
- Optimisation of the spacer geometry is recommended. Compared to aqueous applications, a broad range of potential solutes and solvents in OSN makes the design of spacers for OSN complicated, since the optimised spacers for one application may not be suitable at all for another one. In addition, experimental studies on optimisation of spacer geometry are comprehensively time consuming since the characteristics of the spacers such as void fraction, mesh length, flow angle and filament shape are many and it is difficult to monitor a single characteristic only since these characteristics are often affected each other from a manufacturing point of view. In addition, the interdependence of solution properties and spacer characteristics makes it even more complicated.

Based on the considerations above, software tools for example, a combination of CFD, a tool to simulate the fluid flow, and Aspen, a tool to provide the thermodynamic properties of the solutions, could be used to systematically study the effects of spacer geometry in OSN applications and guide the design of spacer geometry.

- The development of a design programme for OSN applications with pre-defined process targets is needed. Once OSN has demonstrated its potential in chemical industries of interest and a deep understanding of the optimisation of spacer geometry and module configuration is available, the establishment of a suitable programme for OSN process design can smooth the road of the OSN application and guide the process installation.

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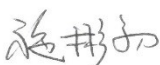
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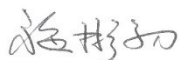
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