ON THE COUPLING OF MEMBRANE TRANSPORT TO HYDRODYNAMICS AND BULK MASS TRANSFER IN REVERSE OSMOSIS: Numerical Modeling and Experimental Studies

Par

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To my parents, José and Carmem.
“Sur l’avenir, tout le monde se trompe. L’homme ne peut être sûr que du moment présent. Mais est-ce bien vrai? Peut-il vraiment le connaître, le présent? Est-il capable de le juger? Bien sûr que non. Car comment celui qui ne connaît pas l’avenir pourrait-il comprendre le sens du présent? Si nous ne savons pas vers quel avenir le présent nous mène, comment pourrions-nous dire que ce présent est bon ou mauvais, qu’il mérite notre adhésion, notre méfiance ou notre haine?”

Milan Kundera

L’Ignorance
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ABSTRACT AND KEYWORDS

Reversible osmosis is worldwide a leading separation process in water desalination, ultrapure water production and other municipal and industrial water applications, as well as a major technology in food processing. Its performance and overall economy are limited by concentration polarization, a natural reversible phenomenon caused by a complex coupling of pressure, hydrodynamic conditions and mass transfer in the feed channel of the membrane module, dependent on the composition of the solution being treated and function, ultimately, of the membrane transport properties. The prediction of the performance of this separation process would be an important advance for process design, control and optimization.

The complexity of the problem is not described by global phenomenological approaches traditional in the membrane field, and for this reason the models based on them cannot accomplish this task satisfactorily and generically. We deal with these problematics and opt to model the fundamental physics behind a pressure-driven membrane separation in liquid phase under non-restrictive assumptions.

The Navier-Stokes equations for the steady laminar cross-flow and the solute conservation equation are solved numerically and simultaneously in a two-dimensional flat channel. The geometry of the channel is limited by either two membranes or by one leaking and one impermeable wall. Solvent and solute transports through the membrane are considered to follow the solution-diffusion model. Rewritten in terms of dimensionless variables and under the Prandtl hypotheses of negligible axial momentum and mass diffusion, the system is solved at each point by a second-order finite difference scheme. Concentrations, permeate flux, rejection rate, field of velocities and pressure are example of parameters which can be calculated at local level.

The membrane solute permeability is an input parameter whose determination is particularly complicated. We develop therefore a bench-scale experimental method enabling the calculation of solute and solvent permeabilities from purely osmotic-diffusive experiments, i.e., when no hydraulic pressure is applied on the membrane, and apply it to reverse osmosis and nanofiltration membrane samples with aqueous salt solutions. It avoids two customary handicaps of other approaches: concentra-
tion polarization if the coefficients are determined in pressure-driven mode, and the neglect of the osmotic flux when the determination is not performed under pressure.

The numerical predictions are validated by comparison to various experimental results from the literature and from our own pilot-scale experiments. In doing so, plate-and-frame and spiral-wound modules with reverse osmosis and tight-nanofiltration membranes are considered for several electrolyte and non-electrolyte solutions. Additional considerations are applied when the flow in spacer-filled channels is simulated. We also evaluate at this stage the adequacy of the permeability coefficients previously determined in osmosis-diffusion for the simulation of pressure-driven separations.

Our simulations highlight the effect of membrane transport on the overall results of the process and the role that permselectivity plays in the complex couplings which we referred to. Parameters to which the permeate flux and the rejection rate show different sensitivities, and the characteristic dependence of the rejection rate on the applied pressure are illustrated for different values of solute permeability. The comparison to experimental results are good and encouraging. The experimental determination of permeability coefficients under the effect of an applied pressure or of concentration gradients uniquely was insightful and did not give totally equivalent results, though yielding good approximate values of solute permeability. We identify limitations of our numerical model and bench-scale experimental method, and propose future research directions. The model and the experimental method are new promising tools with immediate applicability in the membrane field.

**KEYWORDS:** reverse osmosis, nanofiltration, water, desalination, numerical modeling, experimental, concentration polarization, permeability, osmosis, diffusion, spiral-wound membrane, rejection rate, permeate flux, solution-diffusion model
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**Acronyms**

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<th>Acronym</th>
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<tr>
<td>AFE</td>
<td>axial flow exhaustion</td>
</tr>
<tr>
<td>CFD</td>
<td>computational fluid dynamics</td>
</tr>
<tr>
<td>CFR</td>
<td>cross-flow reversal</td>
</tr>
<tr>
<td>CP</td>
<td>concentration polarization</td>
</tr>
<tr>
<td>DNS</td>
<td>direct numerical simulation</td>
</tr>
<tr>
<td>DO</td>
<td>direct osmosis</td>
</tr>
<tr>
<td>DSPM</td>
<td>Donnan-steric-pore-model</td>
</tr>
<tr>
<td>ECP</td>
<td>external concentration polarization</td>
</tr>
<tr>
<td>FO</td>
<td>forward osmosis</td>
</tr>
<tr>
<td>HP</td>
<td>high pressure</td>
</tr>
<tr>
<td>ICP</td>
<td>internal concentration polarization</td>
</tr>
<tr>
<td>IT</td>
<td>irreversible Thermodynamics</td>
</tr>
<tr>
<td>KK</td>
<td>Kedem-Katchalsky model</td>
</tr>
<tr>
<td>LCL</td>
<td>lower confidence limit</td>
</tr>
<tr>
<td>LED</td>
<td>Large eddy simulation</td>
</tr>
<tr>
<td>LR</td>
<td>low recovery</td>
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<tr>
<td>MF</td>
<td>microfiltration</td>
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<tr>
<td>NF</td>
<td>nanofiltration</td>
</tr>
<tr>
<td>ORR</td>
<td>Onsager Reciprocal Relations</td>
</tr>
<tr>
<td>PEG1000</td>
<td>Polyethylene glycol of molar mass 1000 g·mol⁻¹</td>
</tr>
<tr>
<td>PRO</td>
<td>pressure-retarded osmosis</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis</td>
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Glossary

RSS residual sum of squares
SD solution-diffusion model
SK Spiegler-Kedem model
SWM Spiral-Wound module
TFC thin-film composite
TMP transmembre pressure
TSS total sum of squares
UCL upper confidence limit
UF ultrafiltration

Roman Symbols

a activity
A molar membrane solvent permeability (mol·m$^{-2}$·Pa$^{-1}$·s$^{-1}$)
A coefficient of the coefficient matrix
B molar membrane solute permeability (m·s$^{-1}$)
B Berman function
B coefficient of the coefficient matrix
c generalized concentration (mol·m$^{-3}$)
c dimensionless concentration
C dimensional concentration (mol·m$^{-3}$)
C coefficient of the coefficient matrix
d diameter (m)
d flow channel full-height or half-height (m)
D diffusion coefficient (m$^{2}$·s$^{-1}$)
D coefficient of the coefficient matrix
E coefficient of the coefficient matrix
GLOSSARY

$f$ truncation term from an infinite series

$f_P$ polarization factor

$F$ antiderivative

$G$ Green function

$i$ van’t Hoff’s factor

$I_0$ volumetric membrane solvent resistance (Pa·s·m$^{-1}$)

$I_0^{-1}$ volumetric membrane solvent permeability (m·Pa$^{-1}$·s$^{-1}$)

$j$ transverse grid point

$J$ generalized flux

$J$ total of transverse grid points

$k$ mass transfer coefficient (m·s$^{-1}$)

$k$ truncation term from an infinite series

$k$ counting number

$K$ sorption, distribution or partitioning coefficient

$K$ Berman’s or Green’s constant

$l$ membrane thickness (m)

$L$ generalized phenomenological coefficient

$L$ length of the flow channel (m)

$L_{de}$ dead-end length (m)

$M$ mass (kg)

$M$ molar mass (kg·mol$^{-1}$)

$n$ axial grid point

$N$ molar flux (mol·m$^{-2}$·s$^{-1}$)

$N$ dimensionless number

$N$ total of axial grid points

$p$ dimensionless pressure
GLOSSARY

$P$ pressure (Pa)

$P$ generalized membrane permeability (m$^2$·s$^{-1}$)

$Pe$ Péclet number

$q$ total volume flux (m$^3$·m$^{-2}$·s$^{-1}$, m·s$^{-1}$)

$q$ normalized, dimensionless axial flow rate

$R$ universal gas constant (m$^3$·Pa·K$^{-1}$·mol$^{-1}$)

$R$ rejection rate

$R$ constant term of the vector/matrix

$R$ mass transfer resistance (m$^{-1}$)

$R^2$ (R-Square) coefficient of determination of a linear regression

$Re$ longitudinal Reynolds number

$S$ surface (m$^2$)

$Sc$ Schmidt number

$Sh$ Sherwood number

$t$ time (s)

$T$ absolute temperature (K) if not stated otherwise

$u$ dimensionless transverse velocity

$U$ dimensional transverse velocity (m·s$^{-1}$)

$v$ volume (m$^3$)

$V$ volume (m$^3$)

$V$ velocity field (m·s$^{-1}$)

$w$ dimensionless axial velocity

$w_l$ width (m)

$W$ dimensional longitudinal velocity (m·s$^{-1}$)

$x$ dimensionless geometrical coordinate

$X$ dimensional geometrical coordinate (m)
**GLOSSARY**

\[ x \]  molar fraction  
\[ X \]  generalized driving force (gradient)  
\[ z \]  dimensionless geometrical coordinate  
\[ Z \]  dimensional geometrical coordinate (m)  

**Greek Symbols**

\[ \alpha \]  dimensionless pressure drop  
\[ \beta \]  isothermal compressibility (Pa\(^{-1}\))  
\[ \beta \]  reduced volumetric membrane solvent permeability  
\[ \beta^* \]  dimensionless membrane molar solute permeability  
\[ \gamma \]  activity coefficient  
\[ \Gamma \]  concentration polarization modulus  
\[ \Gamma \]  osmotic factor  
\[ \delta \]  quantity lost due to leaks  
\[ \delta \]  boundary layer thickness (m)  
\[ \Delta \]  difference  
\[ \Delta \]  Laplacian (m\(^{-2}\))  
\[ \epsilon \]  criterion of convergence  
\[ \zeta \]  order of approximation/truncation  
\[ \lambda \]  constant  
\[ \Lambda \]  constant  
\[ \mu \]  chemical potential (J·mol\(^{-1}\))  
\[ \mu \]  dynamic viscosity (Pa·s)  
\[ \xi \]  order of approximation/truncation  
\[ \pi \]  osmotic pressure (Pa)  
\[ \Pi \]  osmotic pressure (Pa)
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<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>$\rho$</td>
<td>volumetric mass density (kg·m$^{-3}$)</td>
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<td>$\sigma$</td>
<td>Staverman reflection coefficient</td>
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<tr>
<td>$\sigma$</td>
<td>numerical coefficient</td>
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<tr>
<td>$\tau$</td>
<td>reduced channel length</td>
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<tr>
<td>$\phi$</td>
<td>solvent volume fraction</td>
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<tr>
<td>$\varphi$</td>
<td>membrane layer</td>
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<tr>
<td>$\Phi$</td>
<td>dissipation function (J·m$^{-3}$·s$^{-1}$)</td>
</tr>
<tr>
<td>$\Phi_m$</td>
<td>dissipation function integrated across the membrane (J·m$^{-2}$·s$^{-1}$)</td>
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<tr>
<td>$\chi$</td>
<td>chemical flux (exchange flux) (m·s$^{-1}$)</td>
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<td>$\chi$</td>
<td>numerical coefficient</td>
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<tr>
<td>$\Psi$</td>
<td>stream function</td>
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<tr>
<td>$\omega$</td>
<td>membrane solute permeability (mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$)</td>
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<tr>
<td>$\omega$</td>
<td>relaxation factor</td>
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<tr>
<td>$\omega$</td>
<td>dimensionless domain</td>
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<td>dimensional domain</td>
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**Subscripts**

- *alt* alternative
- *app* apparent, effective
- *av* averaged
- *b* bulk
- *B* Berman
- *conv* convergence
- *CP* concentration polarization
- *diff* diffusion
- *f* free
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<td>Green</td>
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<td>h</td>
<td>hydraulic</td>
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<td>HD</td>
<td>hydraulic dispersion</td>
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<tr>
<td>i</td>
<td>component i</td>
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<tr>
<td>∞</td>
<td>value considered in a limiting case</td>
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<td>inlet</td>
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<td>entrance of the flow channel</td>
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<td>int</td>
<td>intrinsic</td>
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<td>j</td>
<td>transverse grid point</td>
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<td>J</td>
<td>highest transverse grid point</td>
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<td>k</td>
<td>component k</td>
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<td>l</td>
<td>downstream or permeate side</td>
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<td>outlet</td>
<td>exit of the flow channel</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
</tr>
<tr>
<td>p</td>
<td>permeate</td>
</tr>
<tr>
<td>P</td>
<td>downstream or permeate side</td>
</tr>
<tr>
<td>R</td>
<td>upstream or retentate side</td>
</tr>
<tr>
<td>s</td>
<td>solute</td>
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<tr>
<td>thermodynamic</td>
<td>thermodynamic</td>
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</table>
GLOSSARY

\( v \)  solvent

\( vH \)  van’t Hoff

\( W \)  wall

0  initial value

0  upstream or retentate side

0  homogeneous parameter with same value as is in the inlet

*  value corrected for leak

**Superscripts**

†  indicates a value multiplied by \( iRT \) (\( i \): van’t Hoff’s factor)

\(^\wedge\)  molar quantity

\(^\wedge\)  extrapolated value

\( l \)  downstream or permeate side

\( l \)  longitudinal

\( n \)  axial grid point

\( N \)  highest axial grid point

\( osm \)  osmotic

\( t \)  transverse

− (overline)  averaged value

*  local mean value

∼  average

+  concentrated solution

−  dilute solution

0  reference value

0  upstream or retentate side

**Other Symbols**
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<td>$\nabla$</td>
<td>gradient</td>
<td>(m$^{-1}$)</td>
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<tr>
<td>$\mathcal{P}_s$</td>
<td>local membrane solute permeability</td>
<td>(m$^2$·s$^{-1}$)</td>
</tr>
<tr>
<td>$\mathcal{P}_v$</td>
<td>specific membrane solvent permeability</td>
<td>(m$^2$·s$^{-1}$·Pa$^{-1}$)</td>
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CHAPTER 1

Introduction

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1.1 Membranes and Membrane Separation Processes

The separation of the constituents of a fluid mixture can be achieved in principle by benefiting from the differences of transport rates of each element in a suitable medium. One may call this medium a “membrane”. The numerous utilizations of membranes have given rise to a variety of operations eventually designated “membrane separation processes”.

The evolution of the membrane field may be regarded from the point of view of major scientific milestones, usually without any connection between them and dissociated from the notion of membranes we have today, or from the perspective of notable industrial and commercial achievements. The observation of the phenomenon of preferential permeability by Nollet in 1748 is frequently considered the starting point. The investigations of electro-osmosis by Reuss in 1803 and Porret in 1816, of endosmosis and exosmosis by Dutrochet in 1827 and the pioneering works of Graham on dialysis in 1861 complement the set of early observations related to the field. Several relations and theoretical considerations will have contributed to shaping a more delimited area of knowledge: diffusion, by Fick in 1855; osmotic pressure, by van’t Hoff in 1887 and Einstein in 1905; electrolyte transport, by Nernst and Planck in 1889; membrane equilibrium, by Donnan in 1911. Of course, these are just some examples and names. Anyway, it was not until some decades
ago and the development of synthetic polymeric materials, specially of asymmetric membranes by Loeb and Sourirajan in the early 1960s, that membranes started to be systematically applied to customary, standard separations in small and large scales. Microfiltration and ultrafiltration for laboratory applications in 1920 and 1930 and for water purification in the end of World War II, the separation of uranium isotopes by means of gaseous diffusion in the framework of the Manhattan Project from 1942 and at Eurodif’s facility in Pierrelatte (France), and hemodialysis in 1950 are perhaps the operations which inaugurated the technological uses of membrane separation processes [Baker, 2004, pp. 1–3, 97; Böddeker, 1995; Mulder, 1996, pp. 9–12].

Nowadays, membrane processes are state-of-the-art technologies for separations in liquid, gas and vapor phases. They are employed successfully in large scale to desalt seawater and brackish waters, to purify wastewaters, to produce ultrapure water for different industrial sectors, to concentrate and recover valuable substances, to fractionate and concentrate mixtures in the food and pharma sectors etc. Membranes find cutting-edge applications in catalytic membrane reactors, membrane bioreactors, fuel cells, battery separators, in the generation of renewable energy by pressure-retarded osmosis and in the use of protective coatings. In medical applications, membrane separations are the fundamentals of artificial organs (e.g. kidneys and lungs), blood oxygenators and hemodialysis systems as well as of controlled released pharmaceuticals [Baker, 2004, pp. 1–14; Strathmann, 2011, pp. 1–4].

The success demonstrated by membrane processes is not by chance. Membrane separations have many competitive advantages. They can achieve high levels of purification after which only few post-treatments may be necessary. They operate at ambient or moderate temperature, in many instances without addition or generation of hazardous chemicals. Compared to other conventional separation techniques, they are often simpler technically, more energy-efficient and environmentally friendly and typically scalable from very large continuous operations up to batch-wise treatments of small quantities. Not least, membranes can be tailored in order to perform specific separations. All this at cost-advantageous conditions as attest the market growth and lasting scientific interest. Notwithstanding the above, some disadvantages exist. These drawbacks concern for instance the performance limitation induced by natural phenomena such as fouling and concentration polarization (explained further on the thesis), the mechanically fragile structure, membrane aging resulting in drop of performance, low chemical resistance against
organic solvents and extreme pH values, and the important elevation of energy costs under certain conditions (e.g. very high salinity in desalination applications) [Drioli and Giorno, 2009, p. 21; Strathmann, 2011, pp. 1–14].

The course and outcomes of a membrane separation process depend not only on the interactions of each constituent of the mixture among each other but also, and inherently, on the interactions they have with the membrane. All this should be conceived under the influence of one or more driving forces. The split into structure-based membrane categories, driving forces and physicochemical property-based mixture types can be vast. Figure 1.1 presents an overview of widespread membrane separations. Only liquid-phase separations are concerned by this thesis.

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<tr>
<td></td>
<td>isotropic</td>
<td>Dialysis</td>
<td>Electrodialysis</td>
<td></td>
</tr>
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<td>Non- or microporous, with fixed charge</td>
<td>anisotropic, track-etched</td>
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<td>immobilized in isotropic porous membrane</td>
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</tbody>
</table>

Figure 1.1: Membrane separation processes in liquid phase classified by membrane type (columns “Selective barrier” and “Typical structure”) and primary driving force. Note: (i) \( d_p \) is the pore diameter; (ii) pervaporation membranes separate a liquid feed from a vapour phase. Figure from Drioli and Giorno [2009, p. 20].

We focus on barometric separations in liquid phase. They are used to purify or, reciprocally, to concentrate dilute aqueous or non-aqueous solutions by applying a pressure difference across the membrane. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO, termed “hyperfiltration” in the past) are the classic processes of this category. MF is applied for the separation of particles, UF of macromolecules and NF and RO of low molecular weight solutes. Therefore, from MF to RO, the pores of the selective membrane matrix becomes smaller. The application range of these processes is illustrated in Figure 1.2.
CHAPTER 1. Introduction

In this thesis, our particular interest is reverse osmosis. Nanofiltration is treated in part only. Other processes appear incidentally.

Reverse osmosis and nanofiltration require membranes capable of yielding high solvent flux while maintaining high selectivity. Currently, these and other requirements are met for water applications by membranes whose selective structure (barrier layer) is most of the time made of cellulose acetate (first generation material), aromatic or aliphatic polyamide (most frequent case), polyimide or sulfonated polysulfone. The polymers are usually in cross-linked form, i.e. bonded by covalent bonds, avoiding them to solubilize in the solvents. The standard technology consists in forming a thin (100 nm–1000 nm), nonporous (“dense”) layer on the top of a much thicker (100 µm–200 µm), microporous, non-selective layer. Thin-film composite (TFC) membranes are a widespread type of membrane whose barrier layer (20 nm–1000 nm thick) and porous substrate are made of two or more materials with complementary properties. These layered structures, called asymmetric or anisotropic membranes, in contrast to symmetric or isotropic ones which are homogeneous with regard to their composition (30 µm–500 µm thick), represented a breakthrough in the membrane field. Asymmetric membranes ensure high flux because the top layer is thin, and mechanical stability owing to the porous sub-

Figure 1.2: Types of compounds and substances separated by pressure-driven membrane processes in liquid phase. The suitable process is straightly related to the molecular size of the substance(s) to be separated. Figure from Mulder [1996, p. 286].
strate. The membranes are manufactured as flat sheets, hollow fibers, tubes or capillaries [Drioli and Giorno, 2009, pp. 21–22, 30, 36–37; Strathmann, 2011, pp. 21, 147–150].

Water applications are comfortably the main field of application of reverse osmosis. Not long ago [Baker, 2004, p. 221], water desalination accounted for approximately the half of all installed RO systems and the production of ultrapure water for power generation, electronics and pharmaceutical industries for 40%, the remainder concerning specific applications in the food industry and pollution control. The use of reverse osmosis in the desalination industry is so far-reaching as long as the water is not excessively salty (not ≥ 4% in weight) and does not have a too high fouling proneness [Maurel, 2006, pp. 268–269], that it has overtaken thermal desalination processes in terms of the worldwide installed capacity (65% for the former against approximately 30% by 2013) [Glo, 2014]. Nanofiltration does not reduce seawater salinity so as to achieve drinking standards, but does it with mildly brackish waters. NF is more and more widespread as a pretreatment for both RO and thermal distillation desalination since it decreases the scaling and fouling potential of the desalination feeds by removing divalent ions and dissolved organic materials [Greenlee et al., 2009; Schäfer et al., 2005, pp. 331–332]. It also has various niche applications in different sectors of the chemical industry and in the water and food processing branches: concentration of whey, syrups and thin juice; waste water recuperation in the pulp and paper industry; treatment of textile effluents and landfill leachates; recovery of metals and acids in the mining and metal finishing industries; removal of organic and inorganic trace contaminants and many others [Schäfer et al., 2005].

1.2 Motivations and Problem Statement

Many membrane separations are today well-established processes whereas others are still promises for the future. In both cases, the achievements were and are evidently not without troubles and limitations. Anyway, in view of the criticality of the issues they help(ed) to address, like the supply of drinking water, the advances in medical treatments and the production of clean energy, the developments could and should not be delayed. In parallel, work shall be done in order to enhance the performance of existing processes and to supply them with more suitable and fine tools. Our works deal with the latter problematics which we revisit in more detail.
In the previous section, we mentioned that the outcomes of a membrane process depend on the individual components of a mixture (solvents, solutes) and on their interactions with the membrane. In reality, these are two out of three points: the manner the process is carried out is also a key determinant of its results. By this, we mean that operating conditions and equipment specificities affect the process decisively, to a large extent by influencing the first two factors. In principle, everything is intertwined in a membrane separation process, and that is where some difficulties – and opportunities – lie.

Traditionally, the task of modeling membrane filtration is undertaken by phenomenological approaches and by describing the process’ parameters in averaged form. This approaches presents some benefits: ease of implementation, sufficiency for the application(s) they have been thought for, indication of pertinent occurrences or phenomena which might take place. However, they lack generality when other applications are envisioned, are not adequate for making extrapolations for other operating conditions and are restricted in terms of the quantitative analyses they allow to do and the eventual new insights one could gain from them. Briefly, they are neither adequate to simulations nor to making predictions.

From the applied perspective, the total production and the quality of the product are vital sought-after unknowns of a process. For this reason, being able to predict the permeate (or filtrate) flux and the permeate concentration (or rejection rate) at any operating condition would be highly beneficial. In addition to the obvious interest of knowing how much and how good a process can produce, the knowledge of these parameters allow inter alia:

- To appraise the performance of different prospective membranes for a particular application;
- To calculate the membrane surface necessary for achieving the desired permeate flow rate (recovery) or, reciprocally, concentrate generation;
- To define the number of passes that yield the desired product concentration;
- To estimate the energy consumption of the process;
- To calculate membrane and equipment costs;
- To optimize the operating conditions as functions of changing feed characteristics, product specifications or process exigencies;
• To optimize the characteristics (e.g. dimensions and geometry) of membrane modules;
• To reduce the amount of bench-scale and above all pilot experiments during the scale-up of the process, the costs they generate and the time spent with them.

Such a versatile determination or simulation tool with broad and general applicability is not yet available, what justified our research efforts. Progresses are welcome and can difficultly circumvent a good deal of modeling (in an – understandably – very experimental area of knowledge). The task is inherently elaborate and becomes all the more so since two naturally occurring phenomena which reduce the process performance are complex to model: concentration polarization combined with osmosis, and fouling.

After all, the advancement and the outputs of a reverse osmosis process (permeate flux, rejection rate, retentate concentration and flow rate etc.) are a function of the accumulation of solute precisely on the membrane surfaces, essentially on the feed/concentrate side, and, by that means, they are function of concentration polarization (if the accumulation is reversible) and fouling (if the accumulation is irreversible). The membrane surface concentration is determined intimately by the conditions in the flow channel (“above” the membrane): the composition, the concentration itself, the pressure difference across the membrane, the flow velocities, the permeation rate. Some of these parameters are not known in advance and vary spatially all over the channel. Actually, the aim is to calculate all or most of them from known inputs. This is one family of studies. In most cases, this intricate scientific problem is addressed either by classic approaches which have recourse to phenomenological descriptions of the process and to averaged parameters, or by local models based on fundamental principles and rigorous solving of the momentum and mass balance equations in the flow channel. We adopt the second methodology and employ for that our own approach and numerical model. It has been developed for many years in our research group in a perspective of increasing difficulty. Pure hydrodynamic problems and problems combining hydrodynamics and mass transfer for total solute-rejecting membranes in different geometries have already been studied. We are now able to add problematics of membrane transport to them, like the prediction of the rejection rate and the thorough evaluation of the impact of the membrane transport properties on the overall conditions in the feed channel of the membrane module and on the process outputs.
The variables just cited depend yet on the membrane transport parameters, frequently unknown and on top of that influenced by the conditions surrounding the membrane. They are input parameters of some of the models of the foregoing paragraph (the most complete ones), of ours included. Just as it is necessary to know the membrane transport properties related to the permeation of solvent in order to predict the permeate flux, it is not possible to determine the permeate concentration if the membrane transport properties for transmembrane solute transfer remain unknown. Such determinations represent another family of studies. There is a prodigious amount of theoretical, modeling and experimental studies because mass transfer across membranes is it too a complex subject given the numerous coupled phenomena and mechanisms at microscopic scale that determine the macroscopic transport properties. No really “universal” method exists for the time being for determining the macroscopic properties. We opted for an experimental assessment of water and salt permeabilities of some membranes and developed a method for this purpose.

Widespread utilization of simulation methods for industrial and other commercial applications requires predictive capabilities and imposes the validation of all models and experimental methodologies employed. Since scale-up usually results in differences compared to the assumptions and conditions valid for bench-scale experiments and for theoretical studies, the validation of our studies is an integral dimension of this work.

Our study is interdisciplinary in terms of both scope and methodology, content and form. We believe that part of the originality of our work lies in this fact, and that the remainder of it comes from the novel approaches which we propose for achieving our single aims, from the conclusions that we reach and from some of the questions which we raise.

1.3 Aims of the Study

In more practical terms, we intend with this thesis:

- To model numerically and at local level a highly coupled problem which combines the description of the hydrodynamics and mass transfer in the feed channel of membrane modules with the transmembrane solvent and solute transfers. In fact:
This work is an additional development in a long-lasting effort of our research group toward the development of suitable models for the simulation of pressure-driven membrane processes in liquid phase;

Traditional models do not unify these three dimensions of the separation problem, and we believe that they need to be treated together.

- To determine the membrane solute permeability experimentally. More precisely, we want:
  - To develop a bench-scale experimental method based on the natural evolution of the system on its own as a function of spontaneous solute diffusion and osmosis, thus applying no external driving force, and to define a mathematical treatment allowing to extract membrane transport parameters from the experimental results;
  - To evaluate the dependence of these parameters on concentration, which is one of the process’ driving forces;
  - To minimize concentration polarization effects, which lead otherwise to spurious findings and misleading conclusions.

- To validate the numerical model:
  - For different geometries;
  - By comparison with experimental data from the literature;
  - By comparison with results from our own experiments.

- To evaluate the adequacy of the membrane transport parameters determined experimentally in the simulation of reverse osmosis:
  - To conclude about the utility of the method proposed;
  - To conclude about the (in)equivalence of the membrane’s “state” whether it is subject to an applied pressure or not (as in pure osmosis-diffusion).

- To approach the prediction of the outputs of processes carried out with spacer-filled membrane modules.

- To gain new understanding about the coupling between membrane transport, hydrodynamics and bulk mass transfer and have the measure of the effect of certain parameters:
  - By doing targeted sensitivity analyses;
  - By making use of a convenient rationalization of the parameters of the problem all along the thesis.
A challenge we set ourselves was to avoid the use of too many parameters of too difficult determination as far as possible. We were curious to know (and not naive!) how far it would be possible to go like this. Whenever this is not practicable, the predictability of the process outputs is negatively impacted. For similar reasons, we avoided as much as possible the determination of inputs by resorting to outputs.

We focused on reverse osmosis, on aqueous applications and on plane geometry. If at some point similarities with other processes exist, they may be referred to. Nanofiltration is treated in more detail in certain parts of the thesis for the sake of comparison. Other parts of the study may be extended to nanofiltration in the future.

Fouling is not integrated to this study. It is subject of future works by our group.

### 1.4 Organization of the Thesis

Following this Introduction (Chapter 1), the thesis is arranged in three Chapters. They contain all an introductory part, the presentation of the main content, followed by partial conclusions.

Chapter 2 is entirely dedicated to membrane transport. It starts with a literature review. First, membrane transport mechanisms and models are covered. We investigate afterwards the dependence of the membrane transport parameters on several operating variables. We then go on into the literature covering usual methods for the determination of membrane permeability coefficients under different conditions. The review is essentially generic, but it tends purposely to water desalination at times. The second part of this Chapter is entirely dedicated to experimental studies we carry out at bench-scale. They concern the conditioning of membranes and the determination of transport parameters by means of so-called osmotic-diffusive experiments. The underlying mathematical formulation is developed. After presenting the experimental setup, the results are presented and discussed.

Chapter 3 is devoted from beginning to end to the modeling of pressure-driven membrane separation processes in liquid phase. The literature review exposes initially the problematics of concentration polarization and continues with the classic approaches and models of the field. The latter opt for averaged descriptions of the process and contrast with the alternative local approaches, about which we give
some general statements. From then on, we present our approach for the modeling of membrane processes comprehensively. We do it progressively by dividing the final problem in intermediate steps. Pure hydrodynamics precede problems combining hydrodynamics and bulk mass transfer, and these precede the ultimate model coupling the two problematics to membrane transport. Similarly, analytical studies pave the way for the numerical formulation and model. The latter are presented in depth. After that, a simulation study is performed aimed at discussing the highly coupled problem of membrane transport coupled to hydrodynamics and bulk mass transfer.

The forth and last Chapter combines simulation and experiments. It starts by presenting the comparisons of our simulations to experimental results of permeate flux, rejection rate and local profiles from four studies from the literature. Interesting remarks are pointed all along the discussions. They are followed by a brief literature review about spacer-filled channels, spiral-wound modules and the problematics on the modeling of such modules is. It introduces a second category of comparisons, this time regarding spiral-wound modules. The first comparison is done with data from the literature. The subsequent ones concern our own experiments with spiral-wound membranes. The analysis of permeate flux and rejection rate have each their specificities. At this point, we revisit our results obtained in Chapter 2 when we determined the membrane permeabilities by osmotic-diffusive experiments, and integrate them to our discussions about the simulation of rejection rates in pressure-driven mode.

Final conclusions related to the entire study and directions for future research come just after.

The appendices and the unified list of references follow.

A long summary of the thesis is presented at the end in French.
CHAPTER 2

Membrane Transport

2.1 Literature Review

2.1.1 Membrane Transport Mechanisms

2.1.2 Membrane Transport Models

2.1.3 Solute and Solvent Membrane Permeabilities

2.1.4 Determination of Permeability Coefficients

2.2 Permeability Determination via Osmosis and Diffusion

2.2.1 Mathematical Formulation

2.2.2 Membrane Samples

2.2.3 Pressure-Driven Phase

2.2.4 Osmotic-Diffusive Mode

2.3 Chapter Conclusion

The achievements of any model used for predicting the performance of a membrane process depend on the identification and on the evaluation of the transport parameters which describe the transmembrane flows characteristic of the application. This Chapter deals with these questions.

We start by briefly mentioning general transport mechanisms put forward in reverse osmosis and nanofiltration and by reviewing in closer detail the literature pertaining to several classic transport models applied to mass transfer across these membranes.

Next, we analyze the membrane solvent and solute permeabilities which are important transport parameters of most models. The study tends to a certain extent to the context of water desalination. At first, we focus on the dependence of the permeability coefficients on the processes’ driving forces and operating conditions.
Afterwards, we present and discuss frequent methods employed for their determination and identify main drawbacks.

We then explore the alternative method that we propose for the determination of membrane solvent and solute permeabilities based on osmosis and solute diffusion. A traditional structure is followed: we present the mathematical formulation of these problems, the experimental set up and protocol employed and finally the results obtained with commercial reverse osmosis and nanofiltration thin-film composite membranes and sodium chloride solutions. In addition to this, elements of theory and experimental findings during the membrane conditioning phase are approached.

Conclusions on the different topics treated along the pages close the chapter.
CHAPTER 2. Membrane Transport

2.1 Literature Review

2.1.1 Membrane Transport Mechanisms

Many mechanisms can be invoked for explaining membrane transport and selectivity [Soltanieh and Gill, 1981]. Several of them coexist for a given system and they account for the total mass transfer at very different extents [Soltanieh and Gill, 1981; Yaroshchuk, 2001].

A sieve mechanism, for instance, is valid for applications in microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) but fails to discriminate between ions of similar size which are well separated in desalination by reverse osmosis (RO). Inversely, a solution-diffusion mechanism considers that a substance dissolves in the membrane and then diffuses through it down a concentration gradient; it is not suitable for porous matrices but very popular for dense membranes. In NF, a closer look will also put Donnan exclusion\(^1\) and dielectric exclusion\(^2\) forward [Yaroshchuk, 2001]. If a constituent is preferentially sorbed on the membrane layer and then pushed through capillaries by pressure, the preferential sorption-capillary mechanism emerges. Preferential adsorption of a substance could alternatively takes place in sites all across the membrane which, once occupied, hinder the transport of other constituents: solvent clustering or wetted surface mechanism.

Based on these and other mechanisms, several membrane transport models have been developed. We examine some of them in the following section. Since we focus essentially on RO, models appropriate for MF and UF are not reviewed, and only the convective aspect of NF is dealt with. The models were selected based on the importance of their fundamentals, their longtime application in the membrane field and their further employment in this thesis.

2.1.2 Membrane Transport Models

2.1.2.1 The Approach of Irreversible Thermodynamics

Membrane processes are non-equilibrium, \textit{i.e.}, irreversible processes. The unbalances of different potentials (\textit{e.g.} pressure, electrochemical potential and tempera-

\(^1\) Effect of fixed membrane charges on the concentration of mobile ions.
\(^2\) Mobile ions inducing charges on the membrane as a result of the difference between the dielectric constants of the membrane and the solvent.
ture) across and along a membrane are precisely the driving forces that, by engen-
dering fluxes (e.g. volumetric and solute), give rise to the separation. This rationale
set the basis for the application of Thermodynamics of irreversible processes (IT)
to membrane separations. This approach disregards the membrane structure or
transport mechanism, viewing it as a “black box” separating two compartments.
In the following, we limit our analysis to the theory of linear non-equilibrium
Thermodynamics as it is the most commonly applied to membrane transport.

For slow processes, Onsager postulated that linear relations hold between steady-
state fluxes of a substance $i$, $J_i$, and driving forces $X_i$ (e.g. chemical potential
gradient or temperature gradient) and that any flux can be caused not only by
its primary, conjugated driving force but also by all other non-conjugated forces
(coupled phenomena) via the so-called phenomenological coefficients, $L_{ik}$ [Hwang,
2004; Soltanieh and Gill, 1981]:

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \quad (i = 1, 2, \ldots, n) \quad (2.1)$$

The definition of fluxes and forces does not need to be unique and can lead to
numerous terms with many phenomenological coefficients $L_{ik}$ in Equation 2.1.
They must withal satisfy the so-called dissipation function $\Phi$ which expresses,
during the course of an irreversible process, the rate of energy lost per unit volume
due to the increase of entropy [Hwang, 2004; Soltanieh and Gill, 1981]:

$$\Phi = \sum_{i=1}^{n} J_i X_i \geq 0 \quad (2.2)$$

In the case of processes near equilibrium, Onsager proved that the matrix of the
$L_{ik}$ coefficients is symmetric:

$$L_{ik} = L_{ki} \quad (2.3)$$

The above Onsager Reciprocal Relations (ORR) reduce the number of coefficients
governing the system [Hwang, 2004; Soltanieh and Gill, 1981].

In the IT formalism, equilibrium Thermodynamics variables are defined for in-
finitesimal subsystems into which the membrane is split and where local equilib-
rium is postulated. For an isothermal open system in the absence of chemical
reaction or charge effects, only chemical potential gradients $\mu_i$ need to be consid-
CHAPTER 2. Membrane Transport

... ered. In this case, and noting molar fluxes as $N_i$:

$$\Phi = \sum_{i=1}^{n} N_i \nabla (\mu_i)$$  \hspace{1cm} (2.4)

By integrating Equation 2.4 over the membrane thickness $l$ in the $x$-direction (positive from 0 to $l$), for steady fluxes [Hwang, 2004; Soltanieh and Gill, 1981]:

$$\Phi_m = \int_{0}^{l} \Phi \, dx = \int_{0}^{l} \sum_{i=1}^{n} N_i \nabla (\mu_i) \, dx = \sum_{i=1}^{n} N_i \Delta \mu_i$$  \hspace{1cm} (2.5)

For a system with one solvent (subscript $v$) and one solute (subscript $s$), the latter equation reads:

$$\Phi_m = N_v \Delta \mu_v + N_s \Delta \mu_s$$  \hspace{1cm} (2.6)

From the definition of the chemical potential difference between two states for liquids, with $R$ the universal gas constant, $T$ the absolute temperature, $a_i$ the chemical activity of the component $i$ and $\hat{V}_i$ its partial molar volume, $\Delta P$ indicating the pressure difference across the membrane, and for pressure-independent $a_i$ and $\hat{V}_i$:

$$\Delta \mu_i = RT \ln \Delta a_i + \hat{V}_i \Delta P$$  \hspace{1cm} (2.7)

It is possible to write [Soltanieh and Gill, 1981]:

$$\Phi_m = (N_v \hat{V}_v + N_s \hat{V}_s) \Delta P + RT(N_v \Delta \ln a_v + N_s \Delta \ln a_s)$$  \hspace{1cm} (2.8)

Activities can be written as being proportional to molar fractions $x$ by means of the activity coefficient $\gamma$, that is $a = \gamma x$. Considering the osmotic pressure ($\pi$) to follow van’t Hoff’s law (linear on the solute concentration) for a non-electrolyte, applying the Gibbs-Duhem relation for the binary system, noting with an overline (–) averaged values and $c$ concentration values, some approximations are done for low solute concentrations and constant activities coefficients across the membrane [Hwang, 2004; Strathmann, 2011, pp. 53–54]:

$$RT \Delta (\ln a_s) \approx \frac{RT \Delta (\gamma_s x_s)}{\gamma_s x_s} \approx \frac{RT \Delta x_s}{x_s} \approx \frac{RT \Delta c_s}{c_s} = \frac{\Delta \pi}{c_s}$$  \hspace{1cm} (2.9)

$$RT \Delta (\ln a_v) = -\frac{x_s}{x_v} RT \Delta (\ln a_s) \approx -\frac{RT \Delta x_s}{x_v} \approx -\frac{RT \Delta c_s}{c_v} = -\frac{\Delta \pi}{c_v}$$  \hspace{1cm} (2.10)

Defining the “chemical” or “exchange” flux $\chi$ as the difference between the solute...
and solvent velocities within the membrane [Hwang, 2004; Pusch, 1977]:

\[ \chi = \frac{N_s}{\bar{e}_s} - \frac{N_v}{\bar{e}_v} \]  

(2.11)

By noting \( q \) the total volume flux, corresponding to the first expression between parentheses on the right-hand side of Equation 2.8, we can write:

\[ \Phi_m = q \Delta P + \chi \Delta \pi \]  

(2.12)

Comparing to Equations 2.1, 2.2 and 2.3, linear flux equations are obtained for the total volume flux \( q \) and chemical flux \( \chi \) as functions of the applied pressure difference and osmotic pressure difference across the membrane, with \( L_p, L_{px}, L_\pi \) being phenomenological coefficients:

\[ q = L_p \Delta P + L_{px} \Delta \pi \]  

(2.13)

\[ \chi = L_{px} \Delta P + L_\pi \Delta \pi \]  

(2.14)

The linearity and equilibrium conditions underlying these equations are believed not to be verified when convection is a significant part of the total mass transport, specially regarding the solute flux. In such a case, ORR would hold in differential scale only, except for very small gradients and fluxes, and experiments be needed to evaluate the deviations [Soltanieh and Gill, 1981]. It has even been argued that Equations 2.13 and 2.14 would not be applicable even for RO because of the large transmembrane concentration and pressure gradients [Pusch, 1977].

In whatever way, several models have been built upon the previous ideas. The most frequent ones are presented in the coming pages.

### 2.1.2.2 Kedem-Katchalsky Model

A practical model based on the linear IT approach was proposed by Kedem and Katchalsky (KK) in the late 1950s originally for passive transport through biological membranes [Kedem and Katchalsky, 1958]. Ever since, it has been frequently used whenever solvent-solute coupled transfer (convection) takes place.

The key point of the KK model is the integration of Staverman’s adaptation of ORR, i.e. of Staverman’s reflection coefficient\(^3\) [Staverman, 1951], into the ther-

\(^3\) Negative values of \( \sigma \) can be expected when a substance interacts preferentially with the
mododynamic equations as well as the replacement of the exchange flux $\chi$ by the experimentally more convenient solute molar flux $J_s$. The total volume flux $q$ was from then on assimilated to the volumetric solvent flux $J_v$ [Kedem and Katchalsky, 1958; Soltanieh and Gill, 1981; Spiegler and Kedem, 1966]:

$$0 \leq \sigma = \left( \frac{\Delta P}{\Delta \pi_{thermodynamic}} \right)_{J_v=0} \leq 1$$

$$J_v = L_p(\Delta P - \sigma \Delta \pi) \tag{2.15}$$

$$J_s = \omega \Delta \pi + (1 - \sigma) \tilde{c}_s J_v \tag{2.16}$$

where $L_p$ is the “filtration coefficient” or hydraulic permeability, $\sigma = -\frac{L_p \pi}{L_p}$, $\omega = \frac{L_p L_s - L_p^2}{L_p^2} \tilde{c}_s = (L_s - \sigma^2 L_p) \tilde{c}_s$ is the solute permeability at zero volume flux and $\tilde{c}_s$ is, originally, the logarithmic mean solute concentration between both membrane sides. Nonverification of ORR and/or solution nonideality and nondiluteness can lead to distinct reflection coefficients in Equations 2.15 and 2.16 [Friedman and Meyer, 1981; Ghii, 2003]. The definition of $\tilde{c}_s$ notably influences the predictions of the above equations [Soltanieh and Gill, 1981; Waniewski, 1994]. The arithmetic mean is usually suitable for low volume fluxes; for high volume fluxes and low solute permeabilities, the retentate concentration is adequate; in all other cases, $\tilde{c}_s$ lies within these two boundaries\(^4\) [Soltanieh and Gill, 1981]. Actually, the logarithmic and arithmetic means give similar results when the two concentration are not too different.

The degree of semipermeability of the membrane, in other words its capacity of transporting solvent rather than solute, is directly related to Staverman’s coefficient. Accordingly, the osmotic pressure measured experimentally (i.e., the osmotic pressure at which solvent net flow ceases, equal to $\Delta P$ in Equation 2.15) across an imperfect membrane (i.e., which is not totally solute-excluding) is at any time lower than the thermodynamically predicted value, $\Delta \pi_{thermodynamic}$, by a factor equal to $\sigma$. As a matter of fact, Staverman pointed out that the system’s behavior is altered already from time zero with a leaking membrane when compared to a non-leaking membrane. By “leaking” it is meant that, for a totally non-selective membrane, $\sigma = 0$, as opposed to a membrane for which $\sigma = 1$ and hence solute leakage coupled to solvent is banned [Punzi and Muldowney, 1986].

\(\text{membrane material, e.g. in organic solvent filtration [Kocherginsky, 2010].}\)

\(\text{4 In a pore-flow model, } \tilde{c}_s \text{ is reasonably approximated by the feed concentration [Pusch, 1977].}\)
When compared to \( L_p, L_{p\pi} \) and \( L_\pi \) in equations 2.13 and 2.14, KK’s alternative set of coefficients, \( L_p, \sigma \) and \( \omega \) are less concentration-dependent as long as the concentration gradient and volume fluxes are not too large [Spiegler and Kedem, 1966].

### 2.1.2.3 Spiegler-Kedem Model

Explaining that the concentration profile across the membrane changes at different flow rates and that therefore the rightmost term in equation 2.16 does not correctly represents the influence of the solvent flux on the solute flux, Spiegler and Kedem (SK) developed a new model [Spiegler and Kedem, 1966]. Employing less concentration-sensitive parameters, they proposed applying the previous linear relations at differential level:

\[
J_v = P_v \left( \frac{dp^*}{dx} - \sigma \frac{d\pi^*}{dx} \right) \tag{2.17}
\]

\[
J_s = P_s \frac{dc^*}{dx} + (1 - \sigma) \tilde{c}_s J_v \tag{2.18}
\]

where \( p^*, c^* \) and \( \pi^* \) are mean values across \( dx \) and \( P_v = lL_p \) and \( P_s = l\omega iRT \) (if van’t Hoff’s osmotic pressure law, presented in section 3.1.2.3, is considered) are the local solvent and solute permeabilities respectively.

Typically, the equations are integrated across the membrane assuming constant coefficients and fluxes and subject to the concentration boundary conditions \( c = K_s C_R \) on the upstream side (subscript \( R, x = 0 \)) and \( c = K_s C_P \) on the downstream side (subscript \( P, x = l \)), \( K \) being the partitioning coefficient supposed constant. In terms of the rejection rate \( R = 1 - C_P/C_R \), a popular fashion of SK’s equation is obtained:

\[
R = \frac{\sigma \left[ 1 - \exp \left( -\frac{J_v (1 - \sigma) l}{P_s} \right) \right]}{1 - \sigma \exp \left[ -\frac{J_v (1 - \sigma) l}{P_s} \right]} \tag{2.19}
\]

### 2.1.2.4 Solution-Diffusion Model

The preceding flux equations have all cross terms which stem from IT and account for the coupling of flows. If these terms are zero, the basis for the solution-diffusion model (SD) is laid. It was firstly developed by Lonsdale et al. [1965] independently
from IT and became the most widely used model for dense membranes (RO, dialysis, gas permeation, pervaporation etc.) [Wijmans and Baker, 1995].

Postulating that the transport across the membrane takes place by diffusion through a single phase, Fick’s law holds for the unidirectional molar flux of substance \( i \) [Lonsdale et al., 1965; Wijmans and Baker, 1995]:

\[
N_i = -D_{im} \frac{dC_{im}}{dx} \approx -D_{im} \frac{\Delta C_{im}}{l} \quad (2.20)
\]

\( C_{im} \) is the concentration of \( i \) in the membrane (subscript \( m \)) and \( D_{im} \) its diffusion coefficient in it, hereinafter took constant\(^5\). The chemical potential of \( i \) in an ideal, isothermal, incompressible liquid phase without charge effects is:

\[
\mu_i = \mu_i^0 + RT \ln(a_i) + \hat{V}_i (P - P_i^0) \quad (2.21)
\]

where \( \mu_i^0 \) is the reference chemical potential of \( i \) at the reference pressure \( P_i^0 \), \( a_i \) its activity and \( \hat{V}_i \) its molar volume. One of the assumptions of the SD model is that the solutions on both sides of the membrane interfaces, \( i.e. \) in the phase bulk (no subscript) and in the membrane matrix are in equilibrium (subscript \( 0 \) for the feed interface and \( l \) for the permeate interface) [Wijmans and Baker, 1995]:

\[
\begin{align*}
\mu_{i0} &= \mu_{i0m} \quad (2.22) \\
\mu_{il} &= \mu_{ilm} \quad (2.23)
\end{align*}
\]

Combining 2.21 with 2.22 on the retentate interface:

\[
\mu_i^0 + RT \ln(a_{i0}) + \hat{V}_i (P^0 - P_i^0) = \mu_i^0 + RT \ln(a_{i0m}) + \hat{V}_i (P_i^0 - P_i^0) \quad (2.24)
\]

At the permeate interface, there exists a pressure discontinuity from \( P_i^0 \) inside the membrane to \( P_i \) in the permeate bulk (see comments in section 2.1.2.4.1).

\(^5\) The binary diffusion coefficient of the solvent in the membrane, \( D_{vm} \), refers to a fixed coordinate system: the membrane. However, as indicated by Prigogine, in the homogeneous phase composed of the membrane matrix and the solution, if convection exists across the membrane, the system’s center of mass is actually in motion because solution is moving across the membrane. Therefore, in order to employ a diffusion coefficient corresponding to a mass-fixed reference system (comparable to Fickian diffusion), the solvent diffusion coefficient should be rewritten as \( D_{vm}' = D_{vn} (1 - w)^2 \) where \( w \) is the solvent weight fraction in the wet membrane. The correction due to this moving reference frame is more significant for highly swollen membranes [Geise et al., 2014; Paul, 1974, 2004; Pusch, 1986].
Combining 2.21 with 2.23:

$$
\mu^0_i + RT \ln(a_{i_0}) + \hat{V}_i(P^l - P^0_i) = \mu^0_i + RT \ln(a_{i_{lm}}) + \hat{V}_i(P^0 - P^0_i) \tag{2.25}
$$

These two last equations enable to pass from concentrations inside the membrane to concentrations in the neighboring bulk phases via the sorption or partitioning coefficients $K_{i_{0m}}$ and $K_{i_{lm}}$:

$$
C_{i_{0m}} = \frac{\gamma_{i_0}}{\gamma_{i_{0m}}} C_{i_0} = K_{i_{0m}} C_{i_0} \tag{2.26}
$$

$$
C_{i_{lm}} = K_{i_{lm}} C_i \exp \left( \frac{-\hat{V}_i(P^0 - P^l)}{RT} \right) \tag{2.27}
$$

At this point, it is assumed that the partitioning coefficient is independent of the concentration: $K_{i_{0m}}=K_{i_{lm}}=K_{i_{m}}$ [Mulder, 1996]. Equations 2.20, 2.26 and 2.27 give:

$$
N_i = \frac{D_{i_{m}} K_{i_{m}}}{l} \left[ C_{i_0} - C_i \exp \left( \frac{-\hat{V}_i(P^0 - P^l)}{RT} \right) \right] \tag{2.28}
$$

In the state of osmotic equilibrium, $\Delta P = P^0 - P^l$ balances $\Delta \pi = \pi^0 - \pi^l$ and the solvent (subscript $v$) flux vanishes so that:

$$
0 = N_v = \frac{D_{v_{m}} K_{v_{m}}}{l} \left[ C_{v_0} - C_{v} \exp \left( \frac{-\hat{V}_v(\Delta \pi)}{RT} \right) \right] \tag{2.29}
$$

from which:

$$
C_{v_i} = C_{v_0} \exp \left( \frac{\hat{V}_v(\Delta \pi)}{RT} \right) \tag{2.30}
$$

Under the simplification $1 - \exp \lambda \rightarrow \lambda$ for $\lambda \rightarrow 0$ [Mulder, 1996; Wijmans and Baker, 1995] (valid as long as $v_v$ is small, i.e., inferior to 15 vol% [Geise et al., 2011; Paul, 2004; Soltanieh and Gill, 1981]), the classic SD equation for the solvent molar flux is obtained with a unique coefficient, the molar solvent permeability $A$:

$$
N_v = \frac{D_{v_{m}} K_{v_{m}} C_{v_0} \hat{V}_v}{lRT} (\Delta P - \Delta \pi) \equiv A(\Delta P - \Delta \pi) \tag{2.31}
$$

In the case of the solute flux, it is considered that $-\hat{V}_v(P^0 - P^l)/RT$ is a small quantity [Wijmans and Baker, 1995]. In [Kocherginsky, 2010; Lonsdale et al., 1965; Mulder, 1996], this is justified by explaining that the solute chemical potential gradient is virtually insensitive to pressure under usual conditions of pressure except when the solute molar volume is large (e.g. in organic separations [Paul, 2004]).
This would in fact be the reason why “barodiffusion” is not used for achieving separations [Kocherginsky, 2010]. By means of the molar solute permeability, $B$, the classic SD equation for the solute molar flux reads:

$$N_s = \frac{D_{sm}K_{sm}}{l}(C_{s0} - C_{si}) \equiv B(\Delta C) \quad (2.32)$$

According to the SD model, solute and solvent permeate independently, and separation is a function of the rate at which they diffuse through the membrane ($D_{im}$) and of the difference of their solubilities in it ($K_{im}$). As stated by the Gibbs-Duhem equation, the solute permeability depends not only on the solute and on the membrane material, but also on the solvent, because the solubility constant $K_{sm}$ is a function of the solute activity coefficient on the solvent [Kocherginsky, 2010; Wijmans and Baker, 1995]; the reciprocal idea applies therefore for the solvent permeability.

Notorious shortcomings of the classic SD model are the absence of any part of convection in the transfer mechanism, the assumption of concentration-independent permeabilities and the prediction of unitary rejection when $\Delta P \to \infty$ [Paul, 2004].

An improvement over the classic SD formulation is the solution-diffusion-imperfection model [Soltanieh and Gill, 1981]. In order to model the solvent volume flux and solute molar flux, it includes convective effects by introducing a third coefficient corresponding to a coupling transport coefficient:

$$J_v = K_1(\Delta P - \Delta \pi) + K_3\Delta P$$

$$J_s = K_2(\Delta C) + K_3\Delta PC_R$$

$C_R$ is the retentate concentration.

### 2.1.2.4.1 Pressure and Concentration Gradients in the Membrane

Mathematically, equation 2.31 resembles Darcy’s law of fluid motion across porous mediums. Though, the underlying hypotheses of both expressions are fundamentally different [Wijmans and Baker, 1995]. On the one hand, Darcy’s law is closer...
to pore-flow, according to which the concentration is uniform across the membrane, but not the pressure. On the other hand, the SD model considers pressure uniform across the membrane, but not the concentration, and a pressure discontinuity at the permeate interface (Equation 2.25). In the SD approach hence, only a concentration gradient determines the chemical potential gradient across the membrane. Still, the classic SD theory applies to membranes where diffusion is the only transport mechanism, particularly the so-called “dense” membranes. By doing so, it suggests that the pressure difference applied upstream produces a solvent concentration difference inside the membrane and consequently a diffusional solvent flux; this is implied since Equation 2.27.

This pressure-induced diffusive mechanism is treated by Paul [2004]; Paul and Ebra-Lima [1971] who, admitting pressure uniformity inside the membrane at the high pressure value $P^0$, demonstrates mathematically that the pressure jump at the downstream interface reduces the solvent activity within the membrane. He depicts it by saying that the solvent is “squeezed” out of the membrane at that interface, leading a concentration gradient behind it. In other words, concentration, and not pressure, would be the actual driving force for the solvent permeation [Paul, 1974]. Finally, this analysis counters formulations that consider pressure to raise the solvent concentration up to its equilibrium value at the upstream interface, requiring the pressure within the membrane to be at the low pressure $P_l$ [Paul and Ebra-Lima, 1971].

Criticism to the hypothesis of pressure discontinuity is provided by Kocherginsky [2010]. He suggests that an internal pressure gradient does exist in the membrane resulting from mechanical stresses. The latter are functions of the rheological properties of the membrane and of the external pressure difference. Mechanical supporting of the membrane, for example by porous supports, complicates the analysis a step further. Besides, local osmotic pressure gradients within the membrane as a result of interactions between the membrane material and the permeating species should not be ignored, as well as plasticization of the membrane. The solvent flux equation at Equation 2.31 would be:

$$N_v = A(\Delta P - \Delta \pi - \Delta P_m) \tag{2.35}$$

where $\Delta P_m$ is the pressure difference inside the membrane.

The stress of the membrane matrix has also been mentioned by other researchers and attributed to modifications of the polymer chains as a result of the membrane
swelling. This stress is furthermore considered to be transferred to the solution contained in the membrane pores ("swelling pressure"). Finally, they conclude that the pressure inside the membrane must always be higher than the external pressure [Pusch, 1986].

The controversy could be avoided for practical purposes as done by Luo et al. [2011] for instance, who converts pressure and concentration differences inside the membrane by considering \( \Delta C = \rho_v \beta_{vt} \Delta P \) with \( \beta_{vt} \) being the isothermal compressibility of bulk solvent.

Other models exist in the literature, e.g. the preferential sorption-capillary flow model (by Kimura and Sourirajan) for RO which considers viscous water transport and diffusive solute transfer, the finely-porous model or models relaxing ORR [Pusch, 1977; Soltanieh and Gill, 1981], Donnan-Steric-Pore-Model (DSPM) for NF [Schäfer et al., 2005] and approaches based on the generalized Maxwell-Stefan equations for multicomponent coupled permeation [Paul, 2004]. Anyway, compared to the solvent flux, the description of the solute flux seems to be a more complicated task for most approaches.

Classic models enabling to describe the transmembrane solvent and solute fluxes were presented. They use three parameters: solvent and solute permeabilities and reflection coefficient. The dependence of this parameters on concentration, pressure and temperature will be now discussed.

### 2.1.3 Solute and Solvent Membrane Permeabilities

#### 2.1.3.1 Concentration-Dependence of Permeability Coefficients

The transport coefficients of all models above are well-known to vary to different extents with, for instance, concentration, pressure, temperature and obviously the membrane and solution composition. This dependence is more marked across the membrane insofar as the steepest gradients occur in this direction. In long membrane modules, these variations will extend in the longitudinal direction as well. In spite of all that, and mainly owing to limitations in the determination of these dependencies, one frequently resorts to the assumption of constant coefficients, at least within a determined range of conditions.

The flux equations are all the more useful when they enable to calculate fluxes
from the concentrations in the contiguous bulk phases instead of from the concentrations within the membrane. This “conversion” is done by the distribution (partitioning) coefficient of the substance between the surrounding phase and the membrane material (Equation 2.28). In other words, the distribution coefficient is the relative amount of the component in the membrane in equilibrium. This considered, $K_{im}$, just as the diffusion coefficient $D_{im}$, is an intrinsic part of the permeability coefficients. Depending on the system, either partitioning or diffusion prevails in explaining membrane selectivity [Soltanieh and Gill, 1981].

The water uptake rises in more hydrophilic materials and decreases with a higher degree of polymer cross-linking or of crystallinity. This would explain why swelling of RO membranes is usually lower than that of NF membranes, the former possessing a more rigid and cross-linked structure [Drazevic et al., 2014]. For usual polymers, $K_{vm} \sim \mathcal{O}(10^{-1} \frac{g_{water/cm^3 \text{swollen polymer}}}{g_{water/cm^3 \text{solution}}})$ [Geise et al., 2014; Soltanieh and Gill, 1981]; “less water swollen films” have $K_{vm} < 0.35 \frac{g_{water/cm^3 \text{swollen polymer}}}{g_{water/cm^3 \text{solution}}}$ [Geise et al., 2014]; 15 vol% is considered to be a “small” uptake in typical polymeric desalination membranes [Geise et al., 2011]. At the expense of permselectivity, a higher $K_{vm}$ increases the salt partitioning $K_{sm}$ too: more hydrated polymers tend to have higher dielectric constants which in turn favor the solubilization of dissociated salts owing to the superior stabilization of the ions’ charges. The solute uptake also depends on the interaction of the polymer itself with the solute [Yasuda et al., 1968]. Furthermore, the water sorption by a polymer is an increasing function of the water activity in its surrounding medium: as the salt concentration in the solution in contact with the membrane increases, the water activity in the solution decreases and the water content of the polymer is correspondingly reduced (the membrane undergoes “osmotic dehydration” or “de-swelling”) [Geise et al., 2014].

$K_{sm}$ is preponderant in the selectivity towards electrolytes because the variation of the diffusion coefficients among salts is significantly less than that of their solubilities [Soltanieh and Gill, 1981]. $K_{sm}$ for sodium chloride in uncharged membranes of different chemical composition are spread over a range of values from $\mathcal{O}(10^{-2} - 10^{-1} \frac{g_{water/cm^3 \text{swollen polymer}}}{g_{water/cm^3 \text{solution}}})$ [Geise et al., 2014; Soltanieh and Gill, 1981]. A unique partitioning coefficient is adequate for both cation and anion because their concentrations are equal across the membrane. It can be reasonably constant from very dilute over concentration ranges largely exceeding seawater concentration. It follows that the salt permeability in uncharged membranes is expected to vary with the external concentration as a consequence of changes in the salt diffusion
coefficient $D_{sm}$ mainly [Geise et al., 2014; Soltanieh and Gill, 1981]. This scenario can radically change when membrane charge is a concern (e.g. when polymer’s functional groups dissociate) because fixed charges in the polymer exert notable influence on ion sorption, not to mention on water.

Salt diffusion depends on the membrane water content. This has been explained in the literature by the “free volume theory” whereby a molecule’s diffusion coefficient in a polymer/diluent system is related to the average volume $v_{fm}$ not occupied by the polymer molecules:

$$D_{sm} = \lambda_1 \exp \left(-\frac{\lambda_2 v_{min,D}}{v_{fm}}\right)$$

(2.36)

where $v_{fm} \propto K_{vm}$, $v_{min,D}$ is the space and time-fluctuating free volume needed for a molecule to diffuse, and $\lambda_1$ and $\lambda_2$ are adjustable constants\(^7\) [Geise et al., 2013, 2014; Yasuda et al., 1968]. Briefly, when the salt concentration in the external solution increases, the water activity in it decreases and less water sorbs in the polymer; the free volume decreases and consequently the salt diffusion coefficient in the membrane decreases. The same trend is not necessarily verified in charged polymers - cases for which $D_{sm}$ increased under conditions of osmotic de-swelling have been reported. It has also been reported of aromatic polyamide membranes for which the diffusivity raised at higher solution concentration, but no details on the membrane charge were given in [Soltanieh and Gill, 1981]. Typical values for $D_{sm}$ for NaCl in desalination polymers ranges from $\mathcal{O}(10^{-14} \text{ m}^2\text{s}^{-1})$ up to $\mathcal{O}(10^{-9} \text{ m}^2\text{s}^{-1})$. $D_{vm}$ in desalination polymers range from $\mathcal{O}(10^{-11} \text{ m}^2\text{s}^{-1})$ up to $\mathcal{O}(10^{-8} \text{ m}^2\text{s}^{-1})$ [Geise et al., 2014; Kedem and Freger, 2008; Soltanieh and Gill, 1981].

Severe conditions can cause more acute membrane swelling or shrinkage and thereby influence the permeability values more strongly. In addition to the concentration aspects discussed above, these could be for instance extreme pH values or solutes that interact selectively with the membrane and obstruct solvent paths [Kedem and Freger, 2008]. Lastly, though in a different time scales, fouling and membrane ageing also modify the membrane permeability and selectivity.

The results from the cited articles concern very different membrane materials tested in variable conditions and throughout decades.

\(^7\) As most pure polymer matrices are impermeable to pure salt, $v_{min,D}$ is considered to be equivalent to the free volume available for the solvent to diffuse, which is in turn directly proportional to the volume fraction of solvent in the polymer [Yasuda et al., 1968].
2.1.3.2 Temperature- and Pressure-Dependence of Permeability Coefficients

Membranes may also undergo mechanical compaction caused by pressure differences which can modify their thickness \( l \), porosity, pore connectivity, tortuosity and other structural properties [Merdaw et al., 2010]. Note that the membrane thickness under a solvent gradient, its uniformly swollen thickness \( l_w \) and its dry thickness \( l_d \) may significantly differ [Drazevic et al., 2014; Paul, 2004]. A perceptible modification of \( l_w \) at different solute concentrations is not to exclude in light of the above comments on membrane swelling.

In the framework of Einstein’s studies on diffusion, the diffusion coefficient of solute \( s \) in solution, \( D_{sv} \), can be expressed by means of \( f_{sv} \), its friction coefficient with the solvent \( v \): \( D_{sv} = RT/f_{sv} \). This approach stems from the principle that thermodynamic driving forces are counterbalanced by friction forces (supposed concentration-independent [Kedem and Freger, 2008]). From that, equation 2.37 can be written for the solute permeability \( P_{sm} \) of a non-electrolyte in the membrane, in which case \( f_{sm} \), the friction with the membrane, has to be considered:\footnote{Hence, \( D_{sm} \) is an “effective” diffusion coefficient influenced by the three components in the system (solute, solvent and membrane) rather than a binary coefficient}:

\[
P_{sm} = K_{sm} D_{sm} = K_{sm} \frac{RT}{f_{sv} + f_{sm}} \tag{2.37}
\]

[Kedem and Freger, 2008] also suggests a similar dependence for the reflection coefficient:

\[
1 - \sigma = \frac{K_{sm} f_{sv}}{\phi f_{sv} + f_{sm}} \tag{2.38}
\]

where \( \phi \) is the solvent volume fraction in the membrane. Equation 2.37 shows that the permeability is dependent on the temperature and attributes this dependence to the diffusion coefficient. Temperature-dependence for both solvent and solute permeability have also been proposed to follow Arrhenius-type (\( \Lambda T_2 = \Lambda T_1 \exp[\lambda(T_1 - T_2)/T_2] \)) or power-type (\( \Lambda T_2 = \Lambda T_1 [T_1/T_2]^n \)) relations [Merdaw et al., 2010]. The partitioning coefficients could also depend on \( T \).

The effect of the temperature via the viscosity could be partly responsible for this dependence. Diffusion and viscosity are mixed in the phenomenological membrane transport coefficients when these do not make explicit the viscosity term.
2.1.3.3 Permeability of Asymmetric Membranes

In the previous paragraphs, either an homogeneous membrane or the membrane’s active, selective separation layer (or surface, skin layer) is meant by “membrane”. Actually, today’s membranes are very frequently an assembly of at least two layers with extremely different structural and physicochemical characteristics and commonly referred to as “asymmetric” or “composite” membranes. Generically, for a membrane \( m \) composed of \( n \) layers \( \varphi \) in series, overall permeability coefficients\(^9\) for substance \( i \) (solute and solvent), \( P_{i_m} \), are deduced from classic expressions of mass transfer [Elata, 1969; Jagur-Grodzinski and Kedem, 1966; Soltanieh and Gill, 1981; van Daalen and Smit]:

\[
\frac{1}{P_{i_m}} = \sum_{\varphi=1}^{n} \frac{1}{P_{i_m}^\varphi}
\]  

(2.39)

The reflection coefficient \( \sigma_{i_m} \) can be calculated via:

\[
\frac{\sigma_{i_m}}{P_{i_m}} = \sum_{\varphi=1}^{n} \frac{\sigma_{i_m}^\varphi}{P_{i_m}^\varphi}
\]  

(2.40)

Typically, porous supports are non-selective (\( \sigma = 0 \)) but have finite permeabilities. In pressure-driven mode (RO, NF), the membrane is regarded macroscopically as being uniform and global coefficients are customarily employed. An explicit treatment of the membrane’s active and porous layers is yet very usual in the field of osmotically-driven processes like forward osmosis (FO) and pressure-retarded osmosis (PRO).

A comment deserves to be done with relation to the membrane properties and their quantitative dependences on the membrane structure, and this not only for asymmetric membranes. Usually, the studies on membrane properties are performed with small membrane samples. Spatial variation of membrane properties depending on the position, on a same membrane sheet, from which small membrane samples have been taken, has already been studied in the literature and found to be very significant in some cases (more than 20\% for the water permeability and almost 60\% for the salt flux) [Schipolowski et al., 2006]. Differences between membrane batches, conservation and storage techniques and conditions, pre-conditioning protocols, membrane aging and other factors are behind these observations.

\(^9\) Diffusion and partitioning in each layer may obviously vary.
The discussions above are not intended to be all-encompassing but to present frequent aspects and trends. Given the diversity of membrane materials, solutes, solvents, driving forces, operating conditions and others, basic research about the parameter-dependence of membrane permeability is a much more vast and deep domain. One do not always disposes of local investigation techniques neither. For practical process applications and engineering calculations however, a compromise between theoretical and efficient (even sufficient) description must be reached. This sets the tone for the coming section.

Factors upon which the membrane transport parameters are dependent have been presented. We study now the determination of these parameters.

2.1.4 Determination of Permeability Coefficients

From a modeling point of view, if one or more driving forces vanish or are kept constant, the determination of a certain membrane transport coefficient will be probably easier: by changing applied and driving forces in sequence, all the coefficients would be determined. From an experimental perspective however, applying or suppressing a driving force may not possible with the available material, and measuring certain fluxes may also not be viable.

Not least, the state of the membrane-solution system under certain driving forces and boundary conditions may not be the same under other conditions (e.g. with or without $\Delta P$); as a consequence, the transport coefficients determined by means of a certain process might not be perfectly transposable to other processes [Pusch, 1986; Tiraferri et al., 2013; Zelman et al., 1976].

We focus on membrane solvent and solute permeabilities and present below some methods and expressions for their determination. Afterwards, we present and discuss our own method and experiments.

2.1.4.1 Determination in Pressure-Driven Mode

Permeabilities can be determined when the operation is carried out under pressure, as shown in the following.

2.1.4.1.1 Solvent Permeability
The solvent permeability coefficient of a membrane employed in a pressure-driven process in liquid phase is traditionally determined by “filtering” the pure solvent under pressure. The slope of the resulting plot of permeate flux as a function of the transmembrane pressure (TMP) is the membrane hydraulic permeability \((m^2 \cdot s \cdot kg^{-1}, m \cdot Pa^{-1} \cdot s^{-1})\) at the operating temperature. Such a procedure is also part of membrane conditioning protocols (which, by the way, are not standardized [Hussain and Al-Saleh, 2014; Wright et al., 2005]). The coefficient represents the overall membrane solvent permeability irrespective of differences in the permeability of its constituent layers. The determination of the pure solvent permeability by filtering a solution would require the knowledge of concentration polarization (CP), what is all but simple.

The determination of the hydraulic permeability with pure solvent in a prior pressure-driven, RO-type step is also customary for osmotically-driven processes. In such studies, the value thus determined is adopted further on in all calculations [Cath et al., 2006; Lee et al., 1981; Tiraferri et al., 2013].

2.1.4.1.2 Solute Permeability

The determination of the solute permeability in pressure-driven mode is much less straightforward.

In the literature of pressure-driven separations, mathematical relations have been derived with various degrees of assumption from classic membrane models and enable to estimate transport coefficients from steady-state operating conditions and process data, notably from rejection rate and permeate flux at different \(\Delta P\). They have been and are applied to a wide variety of membrane types. Consider:

- No concentration polarization;
- \(C_P = J_s / J_v\), the downstream solute concentration;
- \(R = 1 - C_P / C_R \approx \Delta \pi / \pi_R\), the rejection rate (\(C_R\) is the upstream concentration and \(\pi_R\) the corresponding osmotic pressure);
- \(\bar{c}_s \approx C_R\) as in a pore-flow model;
- \(\sigma = R_{\infty}\), the well-known asymptotic value for \(R\) when \(J_v \to \infty\) by increasing \(\Delta P\) (here, however, as a consequence of the preceding consideration).
The following linear relation is obtained:\(^{10}\)

\[
\frac{1}{R} = \frac{1}{R_\infty} + \left[ \left( \frac{L_\pi}{L_p} - R_\infty^2 \right) \frac{L_p \pi R}{R_\infty} \right] \frac{1}{J_v} \tag{2.41}
\]

Under these considerations, the three transport coefficients of the Kedem-Katchalsky model can be inferred from the slope and intercept of 2.41 together with the determination of \(L_p\) from Eq. 2.15 \([viz. \; J_v = L_p(\Delta P - \sigma \Delta \pi)]\) and the corresponding definition of the solute permeability \([\omega = (L_\pi - \sigma^2 L_p)\bar{c}_s]\). Alternative methods are to reorder Equation 2.16 conveniently in order to find linear relations from whose slopes and intercepts the desired transport coefficients can be extracted [Mulder, 1996; Zelman et al., 1976]. For instance, a plot of \(J_s/\Delta C\) as a function of \(\bar{c}_s J_v/\Delta C\) has the ordinate-intercept \(\omega\) and the slope \(1 - \sigma\).

Pusch’s analogous relation for the Spiegler-Kedem model reads under the same assumptions and for concentration-independent transport coefficients\(^{11}\):

\[
\frac{1}{1 - R} = \frac{1}{1 - R_\infty} - \frac{R_\infty}{1 - R_\infty} \exp \left[ -J_v(1 - R_\infty)l \right] \tag{2.42}
\]

Finally, for the solution-diffusion model:

\[
\frac{1}{R} = \frac{1}{R_\infty} + \left( \frac{B}{R_\infty} \right) \frac{1}{J_v} \tag{2.43}
\]

In experimental works modeled with the solution-diffusion model, \(R_\infty = 1\) is frequently assumed.

Analogous equations for other models are presented in [Pusch, 1977, 1986; Soltanieh and Gill, 1981].

These mathematical relations are commonly used in spite of being non-predictive and of stumbling upon the unavoidable difficulty of quantifying concentration polarization, or of avoiding it experimentally, even though the membrane surface concentration should be used above in \(R\), \(R_\infty\) and \(\pi R\) (the film model, studied in section 3.1.2.1, is frequently employed for taking its effect into account). One may also be operating in a pressure value much before the plateau \(R_\infty\); the rejec-

\(^{10}\) Whether the flux equations are written in terms of concentration or osmotic pressures and depending on the osmotic pressure law employed, the analytical expression of the permeabilities may differ from some multiplying factor from the ones in subsection 2.1.2.

\(^{11}\) In Pusch’s works [Pusch, 1977, 1986], the Spiegler-Kedem equations (2.17, 2.18) are multiplied by \(-1\).
tion plots have indeed a very steep increase from low to intermediate operating pressures. The reality is that concentration polarization is *per se* another complex scientific problem and a core part of this thesis, treated in the two coming chapters.

The use of these non-predictive equations, although successful in different cases, does not give good results always. The neglect, when bulk concentration values are used, of the fact that the concentration on the membrane surface is enhanced due to CP, can be very detrimental to subsequent calculations of rejection rate employing permeabilities thus determined [Zhou and Song, 2005]. If rejections varies considerably with the permeate flux (induced by the operating pressure), one is not working in the rejection-plateau zone and so, unless rejections are too high or too low, the fitting of the above equations to experimental data will be insufficient [Lipp et al., 1994; Nakao and Kimura, 1981]. Sometimes, the ratio $B/R_\infty$ is seen as a modified permeability coefficient [Lipp et al., 1994]; this accounts for the fact that usually $R_\infty \neq 1$ and can give better fittings, but the physical meaning behind is ambiguous.

### 2.1.4.2 Determination Under No Hydraulic Pressure

The solute permeability can be determined when no pressure is applied and the flux of solvent is negligible, but a concentration gradient exists between the sides of a membrane. We imagine two compartments isolated from each other, separated by this membrane and between which no solvent flows. The next lines show it in more detail.

#### 2.1.4.2.1 Pure Solute Diffusion

If a mass balance is written for this unsteady system separated by a solution-diffusion-type membrane of exposed area $S$ with constant solute permeability (and, again, *impermeable* to the solvent), the (not necessarily equal) volumes $V$ of each half-cell remain constant in time $t$, but not the concentrations $C$: \[ V^+ \left( \frac{dC^+(t)}{dt} \right) = -J_s(t)S = -BS[C^+(t) - C^-(t)] \] \[ V^- \left( \frac{dC^-(t)}{dt} \right) = J_s(t)S = BS[C^+(t) - C^-(t)] \] (2.44) (2.45)

Superscripts “+” and “−” correspond to the concentrated and to the dilute solu-
tions respectively. Applying the initial condition $C^+(0) - C^-(0) = C^+_0 - C^-_0$, the time evolution of the system is described by:

$$
\ln \left( \frac{C^+_0 - C^-_0}{C^+(t) - C^-(t)} \right) = BS \left( \frac{1}{V^+} + \frac{1}{V^-} \right)
$$

(2.46)

In this form, this relation has been derived in [Cussler, 2009] in the context of “diaphragm-cell diffusion” and its notation here adapted.

In a typical case, $V^+ = V^- = V_0$ and $C^-_0 = 0$. In this situation, the solute mass balances in the concentrated and in the dilute compartments read respectively:

$$
\ln \left( \frac{C^+_0}{2C^+(t) - C^+_0} \right) = \left( \frac{2BS}{V_0} \right) t
$$

(2.47)

$$
\ln \left( \frac{C^+_0}{C^+_0 - 2C^-(t)} \right) = \left( \frac{2BS}{V_0} \right) t
$$

(2.48)

These linear relations, under other considerations/forms, have been used some times in the literature for determining $B$ (e.g. [Geise et al., 2013; Yaroshchuk, 2010; Yasuda et al., 1968]).

### 2.1.4.2.2 Direct Osmosis

We have just seen the case where a concentration difference between both membrane sides engenders the flow of solute only, but not of solvent. Now, the flux of solvent is integrated to the analysis.

The so-called “direct osmosis” (DO) tests, which in usual terms do not exclude transmembrane solute transport\footnote{Therefore, the term should not be understood as “pure osmosis”.}, are much less plebiscited than the foregoing pressure-driven relations for the determination of transport parameters. Experiments for the determination of the solvent permeability in systems under solely a concentration gradient are uncommon in the literature. This approach is one of the objectives of our studies. In Ghiu [2003], some studies under different conditions are reviewed; other examples can be found in Ghiu et al. [2002]; Goosens and Van Haute [1978]. The permeabilities are derived, for instance, from best-fitting equations adjusted numerically or graphically to experimental data modeled as to follow diverse membrane transport models, or by the steady-state time-lag equations (examples in Soltanieh and Gill [1981]) for the determination of diffusion coefficients combined with the separate determination of the equilibrium parti-
tioning constant by means of sorption experiments. Their conclusions are very
different and frequently compared to transport parameters determined in RO-
mode. Permeabilities in DO have been found to be higher, lower or equivalent to
the corresponding values determined in RO.

2.2 Permeability Determination via Osmosis and
Diffusion

We present in the following pages our alternative approach for the determination of
solute and solvent permeabilities (within the context of direct osmosis, paragraph
2.1.4.2.2).

2.2.1 Mathematical Formulation

The assumption of constant volume of the concentrated and dilute solutions con-
sidered in paragraph 2.1.4.2.1 is not consistent with a more general scenario of
non-negligible osmotic pressure and/or solvent permeability: neither pure solute
diffusion – therefore relations 2.44 – 2.48 are not totally adequate – nor of pure
osmosis.

We consider the more general situation of an isothermal system in transient state
composed of two half-cells containing each a liquid solution of the same solute and
solvent and separated by a membrane permeable to both substances through a
solution-diffusion mechanism c.f. Equations 2.31 and 2.32. The only driving force
is the transmembrane osmotic gradient. The solutions are stirred so as to neglect
both the mass transfer resistances in the boundary layers on the two membrane
sides (external concentration polarization (ECP)) and any natural convective flow
due to buoyancy forces resulting from local density variations with concentration
[Lee et al., 1981; Pedley, 1980]. Figure 2.1 represents this system.

Two interdependent, anti-parallel 1-D transmembrane fluxes exist: the (volumet-
ric) solvent osmotic flux, \( J_v(t) \), and the molar solute flux, \( J_s(t) \). The first accounts
for the volume changes of both compartments, and both the first and the second
for the concentration changes of each solution as time \( t \) elapses. The membrane
is assumed to have constant overall solute and volumetric solvent permeabilities,
Figure 2.1: Schematic representation of the double stirred diffusion cell where two solutions of different concentrations are separated by a semi-permeable membrane.

$B$ and $I_0^{-1}$ during a single experiment$^{13}$. As a result, the concentration gradient across the membrane is constantly changing. The membrane area exposed to the solutions is $S$. Osmotic pressures follow van’t Hoff’s law (section 3.1.2.3). Superscripts “+” and “−” denote respectively the concentrated and the dilute solutions. We write:

$$J_v(t) = -(I_0^{-1})^\dagger[C^+(t) - C^-(t)] \quad where \quad (I_0^{-1})^\dagger = (I_0^{-1})iRT$$  \hfill (2.49)

$$J_s(t) = B[C^+(t) - C^-(t)]$$  \hfill (2.50)

In so doing, we ignore in 2.49 any contribution of the solute to the volume of the solutions as well as the effect – compared to $\Delta \pi$ – of the hydrostatic pressure engendered by the column of liquid resulting from the level difference in the compartments. The solvent and solute mass balances in the dilute half-cell read:

$$J_v(t) = \frac{1}{S} \left( \frac{dV^-(t)}{dt} \right)$$  \hfill (2.51)

$$J_s(t) = \frac{1}{S} \left( \frac{d[C^-(t)V^-(t)]}{dt} \right) = \frac{1}{S} \left( C^-(t) \frac{dV^-(t)}{dt} + V^-(t) \frac{dC^-(t)}{dt} \right)$$  \hfill (2.52)

Combining 2.49 with 2.51 and 2.50 with 2.52:

$$\frac{dV^-(t)}{dt} = -(I_0^{-1})^\dagger S[C^+(t) - C^-(t)]$$  \hfill (2.53)

$$C^-(t) \frac{dV^-(t)}{dt} + V^-(t) \frac{dC^-(t)}{dt} = BS[C^+(t) - C^-(t)]$$  \hfill (2.54)

In the concentrated half-cell and changing superscripts to “+”, the system of

$^{13}$ As overall, global permeability coefficients are considered here (cf. Equation 2.39), and not only the permeability of the solute-rejecting layer, the method is also valid for asymmetric membranes for which, otherwise, internal concentration polarization (ICP) within the different membrane layers and the membrane orientation would be a concern [Lee et al., 1981; Loeb et al., 1997; Yaroshchuk, 2010].
equations is written:

\[
dV^+(t) = (I_0^{-1})^\dagger S[C^+(t) - C^-(t)] \tag{2.55}
\]

\[
C^+(t) \frac{dV^+(t)}{dt} + V^+(t) \frac{dC^+(t)}{dt} = -BS[C^+(t) - C^-(t)] \tag{2.56}
\]

In all cases, we come back to equations 2.44 and 2.45 if \((I_0^{-1})^\dagger = 0\).

For both solutions, the time-evolution of the concentrations and volumes depends solely on their initial values and on the membrane permeabilities. The two parameters being bound, it would be of interest, before solving the system of equations they are governed by, to track the mutual “path” followed by concentrations and volumes in either compartments. Superscript “±” indicates that either solution is considered. Noticing that:

\[
dC^\pm(t) \frac{dV^\pm(t)}{dt} = \frac{dC^\pm(t)}{dt} / \frac{dV^\pm(t)}{dt} \tag{2.57}
\]

it follows from 2.53 and 2.54 or 2.55 and 2.56:

\[
\frac{dC^\pm(t)}{dV^\pm(t)} = \frac{1}{V^\pm} \left( \frac{B}{(I_0^{-1})^\dagger} + C^\pm(t) \right) \tag{2.58}
\]

A particular experiment could start with pure solvent in the dilute side:

\[
C^-(0) = C^-_0 = 0 \tag{2.59}
\]

\[
V^-(0) = V^-_0 \tag{2.60}
\]

\[
C^+(0) = C^+_0 \tag{2.61}
\]

\[
V^+(0) = V^+_0 \tag{2.62}
\]

Applying these initial values, we get:

\[
C^-(t) = \frac{B}{(I_0^{-1})^\dagger} \left( \frac{V^-_0}{V^-(t)} - 1 \right) \tag{2.63}
\]

\[
C^+(t) = \frac{B}{(I_0^{-1})^\dagger} \left( \frac{V^+_0}{V^+(t)} - 1 \right) + C^+_0 \left( \frac{V^+_0}{V^+(t)} \right) \tag{2.64}
\]

The slope \(B/(I_0^{-1})^\dagger\) of Equation 2.63 is especially practical for gaining quick insight into the membrane permselectivity.

We follow an analogous reasoning for the case of a system following the Kedem-
Katchalsky transport mechanism in Appendix A.

The time evolution of the concentration and the volume of the dilute solution is obtained by solving the system composed of Equations 2.53 and 2.54, and of the concentrated solution by solving Equations 2.55 and 2.56. Alternatively, it is possible to get the expressions for the other solution by solving the system of equations of one of them and writing a mass balance for the solvent and the solute in the entire system:

\[
V^{-}(t) + V^{+}(t) = V_{0}^{-} + V_{0}^{+} \quad (2.65)
\]
\[
V^{-}(t)C^{-}(t) + V^{+}(t)C^{+}(t) = V_{0}^{-}C_{0}^{-} + V_{0}^{+}C_{0}^{+} \quad (2.66)
\]

With the previous two equations and by rearranging Equation 2.53 and Equation 2.54 (dilute compartment), it is possible to isolate the derivatives of volume and concentration for the dilute solution. We get the system of first-order linear ordinary differential equations with variable coefficients:

\[
\frac{dV^{-}(t)}{dt} = (I_{0}^{-})^{\dagger}S \left( \frac{V^{-}(t)C^{-}(t)}{V_{0}^{+} + V_{0}^{-} - V^{-}(t)} + C^{-}(t) - \frac{V_{0}^{+}C_{0}^{+} + V_{0}^{-}C_{0}^{-}}{V_{0}^{+} + V_{0}^{-} - V^{-}(t)} \right) \quad (2.67)
\]
\[
\frac{dC^{-}(t)}{dt} = (I_{0}^{-})^{\dagger}S \left( \frac{C^{-}(t)[V_{0}^{+}C_{0}^{+} + V_{0}^{-}C_{0}^{-}] + C^{-}(t)^{2}[V_{0}^{+} + V_{0}^{-}]}{V_{0}^{+} + V_{0}^{-} - V^{-}(t)} \right) + BS \left( \frac{V_{0}^{+}C_{0}^{+} + V_{0}^{-}C_{0}^{-} + C^{-}(t)[V_{0}^{+} + V_{0}^{-}]}{V^{-}(t)(V_{0}^{+} + V_{0}^{-} - V^{-}(t))} \right) \quad (2.68)
\]

Alternatively, one can solve this equations in order to determine unknown parameters. The sought-after values \( B \) and \((I_{0}^{-})^{\dagger}\) can be estimated by fitting them to experimental data. We employed a fourth-order Runge-Kutta scheme [Abramowitz and Stegun, 1972, pp. 897] for the resolution of the system of equations, implemented with a fixed time step of 300 s in the software Microsoft Excel 2010, and fitted values visually, the effect of the solute permeability on the variation of the volumes being very little.

In the coming pages, we apply this treatment to the determination of water and salt permeabilities with our own experiments with RO and NF membranes. These experiments have to phases: a prior conditioning phase followed by the osmotic-diffusive experiments. We first present the experimental protocol and results relative to the membrane conditioning and the determination of the solvent perme-
ability in pressure-driven mode. Afterwards, the the experimental protocol and results relative to the osmotic-diffusive determinations of the solute and solvent permeabilities are presented. Previously, let us present the membrane samples that we used.

2.2.2 Membrane Samples

Pre-cut commercial flat-sheet polyamide thin-film composite (TFC) membrane samples manufactured by Dow Filmtec (United States of America) were employed: BW30 (RO-type) and NF270 (loose-NF-type). These asymmetric membranes have two apparent sides: a shiny, active side and a dull, substrate side. As already mentioned, the active layer faced the feed stream in pressure-driven mode and the concentrated solution in the osmotic-diffusive experiments.

In pressure-driven operation, the BW30 RO membranes are typically recommended for brackish water applications and achieve high salt rejection. For the spiral-wound module BW30-4040, the manufacturer’s data-sheet indicates 99.5% rejection and a permeate flow rate of 50 L·m\(^{-2}\)·h\(^{-1}\) (15% recovery) for an aqueous solution with 2000 ppm NaCl at 15.5 bar and 25°C [Dow, a].

The NF270 NF membranes achieve high rejection of organic compounds but only partial water softening and low salt rejection, being indicated to surface and groundwater applications. A study in laboratory-scale with the NF270 membrane yielded rejections as low as 2.3%-10.9% at 2 bar and 11%-29% at 9 bar (permeate flux from 20 L·m\(^{-2}\)·h\(^{-1}\)-110 L·m\(^{-2}\)·h\(^{-1}\)) with aqueous solutions of NaCl of 5000-25000 ppm at ambient temperature [Hilal et al., 2005].

2.2.3 Pressure-Driven Phase

We present now the membrane conditioning phase and the determination of the solvent permeability under pressure. These experiments were carried out at Institut Européen des Membranes (acronym: IEM) (Montpellier, France) with the kind material support of Prof. Marie-Pierre Belleville.
2.2.3.1 Materials and Methods: Cross-Flow Filtration Unit and Membrane Conditioning

The laboratory-scale cross-flow filtration unit (GE Osmonics SEPA CF II, United States of America) shown in Figure 2.2 was used. Its cell body consisted of two stainless steel parts, bottom and top, measuring 21.3 cm × 16.51 cm × 5.0 cm each. For each experiment, a 18.6 cm × 13.7 cm membrane sheet surrounded by a Viton joint was placed horizontally in the cell body bottom and held in position by four guiding pins; a second O-ring limited the effective membrane filtration area to approximately 132 cm² (an almost rectangular form of 14.4 cm × 9.4 cm if not for its convex rounded corners). In this zone, the membrane lay between a 1.1938 mm (47 mil\textsuperscript{14}) high net-type feed spacer facing its active side and installed in the central cavity of the cell body bottom, and a thin permeate carrier facing its porous support placed in the slight recess of the cell body top. This latter assemblage (without the membrane) can be visualized in Figure 2.2b. The cell body parts assembled together were then inserted between the two parallel blocks of an aluminum cell holder (28.0 cm × 20.0 cm × 20.0 cm) and clamped together. The holder was pressurized by a hand pump (Enerpac P142, United States of America).

A positive displacement pump (Hydra-Cell M13MRSEHHEY, United States of America) whose motor (Lafert ST 90LS4, Italy) was equipped with a variable-frequency drive (ABB ACS 200, Switzerland) fed into the filtration unit ultrapure water kept at 25 °C ± 1 °C in a jacketed tank connected to a temperature-controlled water circulator (Julabo F32, Germany). The feed entered the unit through the slit-shaped cell body bottom’s inlet at 4.1 L·min\textsuperscript{-1} and 0.8 m·s\textsuperscript{-1}. The membrane active layer was always oriented such that it came into direct contact with the feed stream. A cross-flow resulted: the “retentate” flowed back to the feed tank and the permeate, after flowing through the permeate carrier towards the perforated central area on the upper surface of the cell body top, flowed out of the unit into the filtrate collection vessel for continuous weighting by an analytical balance (Precisa XT 4200C, Switzerland) connected to a data acquisition software. A permeate control valve together (with a pressure gauge positioned right before it) and the pressure gauge on the pump discharge allowed to manually modify and to calculate the transmembrane pressure.

Each membrane was conditioned for about 2.5 hours (Figure 2.2c). Initially, a

\textsuperscript{14} “mil” denotes a thousand of inch (0.0254 mm).
“washing” cycle aimed at removing residual chemicals from the manufacturing process and preservatives [Wright et al., 2005] was carried out at low pressure for about 10 minutes. Next, the transmembrane pressure was smoothly increased by increments up to approximately 25 MPa, kept in this condition for about 1 hour, and eventually decreased by increments back to zero. The intermediate pressure stages lasted between 5 and 10 minutes.

2.2.3.2 Results and Discussions: Membrane Conditioning and Solvent Permeability in Pressure-Driven Mode

Figure 2.3 shows the permeate fluxes obtained with both membranes during the three phases of the conditioning process with pure water: initial washing at lowest pressure, increasing-pressure cycle up to $\Delta P \sim 25$ MPa and decreasing-pressure cycle. The transmembrane pressure is defined as $\text{TMP} = \Delta P = (P_{\text{inlet}} - P_{\text{outlet}})/2$ where $P_{\text{inlet}}$ and $P_{\text{outlet}}$. The fluctuations seen in gray are for the most part due to random mismatches between the sampling frequency of the data acquisition software connected to the analytical balance which weighted the permeate and the frequency at which the permeate dripped from the system’s outlet onto the collection vessel; higher fluctuations are due to brief pressure oscillations caused by valve sticking. The permeate flux in black results from a 5-adjacent-points averaging routine for curve-smoothing performed with the software Origin 9.1.

As expected, the permeate flux increased with TMP and was much higher for the NF membrane at same operating conditions. Higher TMP was necessary with the BW30 membrane in order to produce the first permeate when compared to the NF270 sample. At higher pressure differences, it is possible to notice a slight
but continuous decrease of the permeate flux of NF270 with time. This tendency
could be related to a lowering of the hydrodynamic permeability when the mem-
brane undergoes pressurization, possibly due to membrane compaction (cf. section
2.1.3.2). The effect is pronounced for membranes with “more open structure” and
higher water content [Pusch, 1986] which is the case of NF membranes when com-
pared to RO membranes (cf. 2.1.3.1, [Drazevic et al., 2014]). Similar behavior
with other membranes is reported in the literature [Hussain and Al-Saleh, 2014;
Hussain et al., 2013]. At about 6200 s, the permeate flux with the NF270 started
to increase again; we attribute it to a momentary increase of the feed temperature
caused by a brief malfunction of the temperature-controlled water circulator.

In Figure 2.4, lower and upper confidence limits (LCL and UCL) for the water per-
meability $I_0^{-1}$ are computed using Student’s $t$-statistics with confidence intervals of
95%\(^{15}\). The light-blue stripes are “prediction” bands within which lie the images
of the regression lines comprised between $(I_0^{-1})'$s LCL and UCL. $R^2$ (R-Square) is
the coefficient of determination of the linear regressions\(^{16}\). For both membranes,
there is a clear difference between the water permeability values in the increasing-
and in the decreasing-pressure cycles as illustrated in Figure 2.4. The modification
of the membranes in the course the conditioning process is evident and they do
not recover their initial condition once the conditioning is finished. The variation
of the slopes with TMP is particularly apparent during the increasing-pressure
phases and even more in the case of the RO membrane. In our case, even though
the permeability decreased for the NF270 membrane when TMP was increased and
nearly kept its highest-pressure value when TMP was decreased, it increased with
TMP for the BW30 membrane, the value of the permeability at highest pressure
having been kept when TMP was decreased afterwards.

Table 2.1 summarizes the permeabilities $I_0^{-1}$ determined for both membranes. Only
data of the decreasing-pressure cycles were included for this determination because,
for purposes of calculation of $I_0^{-1}$ over a large pressure range, the membranes were

\(^{15}\) Generated with the software Origin 9.1.

\(^{16}\) The linear regressions, generated with the software Origin 9.1, are performed by minimizing
the Chi-square value, i.e., the sum of the squared distances of the fit to each data point, weighted
by an estimation of the standard deviation. When the fitting is weighted with the y-error values
(vertical error), the weights are defined as the inverse of the error so as to give more “weight”
in the fitting to data points with smaller errors. $R^2$ is comprised between zero and unity and
is defined as $1 - RSS/TSS$ where $RSS$ is the residual sum of squares (weighted sum of the
squares of the vertical deviations from each data point to the fitted line) and $TSS$ is the total
sum of squares (weighted sum of the squares of the vertical deviations from each data point to
the mean).
Table 2.1: Membrane water permeabilities determined in pressure-driven mode during the decreasing-pressure phase of the conditioning cycle. The mean value and the 95\% lower and upper confidence limits (LCL and UCL) are presented.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$I^{-1}$ (m·Pa$^{-1}$·s$^{-1}$)</th>
<th>95% LCL</th>
<th>95% UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW30</td>
<td>$8.74 \times 10^{-12}$</td>
<td>$8.70 \times 10^{-12}$</td>
<td>$8.78 \times 10^{-12}$</td>
</tr>
<tr>
<td>NF270</td>
<td>$5.72 \times 10^{-11}$</td>
<td>$5.71 \times 10^{-11}$</td>
<td>$5.73 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

considered to have attained their final conditioning state after the highest pressure stage.

For illustrating our comments on the crucial influence of the conditioning process, two examples are given. The water permeability of the BW30 calculated from the first condition of TMP ($5 \times 10^5$ Pa, approximately 1/5 of the maximum pressure used) and permeate flux of the increasing-pressure cycle would be $4.08 \times 10^{-12}$ m·Pa$^{-1}$·s$^{-1}$, that is, a relative error of $-53\%$ compared to the value in Table 2.1. The water permeability of the NF270 calculated with the values of the increasing-pressure cycle up to TMP = $12.4 \times 10^5$ Pa (approximately 1/2 of the maximum pressure used) would be $6.91 \times 10^{-11}$ m·Pa$^{-1}$·s$^{-1}$, that is, a relative error of $+21\%$ compared to the value in Table 2.1.

It is frequently reported that membrane compaction caused by the applied pressure reduces the permeate flux and improves salt rejection [Dow, e; Fuls et al., 1992; Hussain and Al-Saleh, 2014]. Would the membrane be regarded as a mass transfer resistance proportional to the membrane thickness $l$ only, the influence of TMP on $l$ as an isolated parameter would contradict this well-known operational finding because $l$ would be logically expected to decrease at higher pressures and therefore raise the water permeability value. However, pressure is believed to affect also the porosity of the membrane’s active layer at large: number of pores, their size and size distribution. It has been suggested that higher pressures could open pores on the membrane’s skin as well as connect paths in the polymeric network, which would otherwise be inactive for solvent (and solute) transfer, even when thinking of the (sub)nanometric voids/pores of polymeric materials of RO membranes. These latter ideas could underlie the behavior of the BW30’s permeability. We furthermore believe that each membrane has a transitional pressure range from which compaction and permeability-lowering will always be a concern, even for more rigid materials. We have yet seemingly not reached this value$^{17}$.

$^{17}$Besides, we could think that RO membranes are designed for withstanding generally much higher pressures than the TMP used here.
The activation of new pores would be less pressure-sensitive for membranes with bigger pores [Kosutic et al., 2000]. As for the NF270, the hypothesis of compaction seems thus the most credible in light of the notions previously evoked. The extent of all these effects - and accordingly the water permeability value of a membrane - is in all likelihood dependent on the maximal transmembrane pressure employed during the membrane conditioning process.

### 2.2.4 Osmotic-Diffusive Mode

We present now the osmotic-diffusive experiments and the determination of the corresponding solute and solvent permeabilities. These experiments were carried out in the Chemical Engineering pilot hall of École Centrale de Marseille at the university campus of Saint-Jérôme (Marseille, France). We had the material support of Prof. Olivier Boiron and Prof. Yannick Knapp from Institut de Recherche sur les Phénomènes Hors Équilibre (acronym: IRPHE) (Marseille), who kindly provided us with the diffusion cell.

#### 2.2.4.1 Materials and Methods: Double Stirred Diffusion Cell and Osmotic-Diffusive Determinations

The double stirred diffusion cell apparatus schematized in Figure 2.5 and shown in Figure 2.6 was used. It has two separate half-cells in the form of right rectangular prisms. Each of these compartments is 8.0 cm high. Their bases are 5.0 cm (direction perpendicular to the membrane position) and 4.0 cm (parallel to the membrane) wide. Their thick walls are made of acrylic and glued on each other tightly; the lines defined by the contacting surfaces were sealed with silicone sealant on the side turned to the half-cell’s exterior.

Two vertical apertures (1.0 cm of diameter, center positioned 1.9 cm above the base) located at symmetrical positions, one in each compartment, and the channel in-between are the unique communication between the two half-cells. In one of the compartments, the aperture is drilled in an horizontal cylinder-shaped projection (0.25 cm high, 3.5 cm of diameter) on the outer side of the wall; in the other half-cell, it is drilled in an horizontal cylinder-shaped depression on the outer side of the wall. The zone comprised between the aperture and the interior of the respective half-cell is limited by a funnel-shaped channel pierced all along the half-cell’s wall (Figure 2.6b). This channel’s constant cross-sectional part (“stem”) is 0.5 cm long.
(a) BW30 membrane (RO).

(b) NF270 membrane (NF).

Figure 2.3: Pure water permeate fluxes at different transmembrane pressures set along the membrane conditioning process.
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(a) BW30 membrane (RO).

(b) NF270 membrane (NF).

Figure 2.4: Permeate flux as a function of transmembrane pressure during the membrane conditioning process.
and has a diameter of 1.0 cm (as does the aperture); its variable cross-sectional portion ends at the inner side of the compartment’s wall with a diameter of 2.0 cm. When the half-cells are assembled together, face-to-face, the resultant form of the connected funnel-shaped channels resembles a nozzle.

A membrane sample (previously conditioned) with a diameter of 3.5 cm was placed in the depression of the left half-cell, which is the area where the depression and the projection of the other compartment come into touch. In this area, two rubber O-rings, one in the projection and one in the depression, each partially embedded in their grooves and with 2.9 cm of diameter, secured the membrane in position when the device was assembled and prevented the establishment of communicating vessels between the two compartments. The membrane surface $S$ exposed to the solutions had a diameter $d_m$ of 1.0 cm for an area of 0.785 cm$^2$, just as the aforementioned apertures and stems.

Six bolt-and-nut assemblies, three in the front and three in the back of the apparatus, fastened the half-cells together. Once assembled, the apparatus was placed between two thick acrylic blocks whose mutual distance could be adjusted by sliding them along threaded rods and fixed at the desired position (here, touching the compartments) by a bolt-and-nut set at each side so as to clamp the cells together. A lid prevented the loss of water by evaporation in the compartments and housed the gear of the stirring system$^{18}$. A regulated power supply of 1.3 V fed a small motor placed on the top of the lid and rotated the agitators in each half-cell at approximately 120 rpm.

Before each experiment, leakproofness around the O-rings and junctions was systematically checked. Once the membrane was in place, a compartment was filled with pure distilled water, the other remaining empty, and a visual check for leaking done after 20 minutes. Afterwards, the water-containing compartment would be emptied out and wiped, and the other half-cell filled with water for a visual check for leaking after renewed 20 minutes.

An experiment started by filling both cells simultaneously. Initially, the left one, named “concentrated” compartment further on in the text, contained $\sim$ 100 mL of a sodium chloride (reagent grade, Honeywell Seelze, Germany) solution prepared with distilled water; the right one, i.e. the “dilute” half-cell, contained $\sim$ 100 mL of

---

$^{18}$ The lid had two holes at each side which enabled access to the solutions without taking off the lid. This functionality was neither necessary nor used in our experiments, reason the holes were plugged with rubber corks.
pure distilled water. No recirculation or pumping system existed. The membrane active layer was always oriented such that it came into contact with the concentrated solution. Each experiment lasted for between 5 and 15 days depending on the measurability of the evolution of the concentration in the dilute compartment (measurements with higher sensitivity) and on the height of liquid in the compartments (for preventing overflow in the dilute side and ensuring the membrane is submerged in the concentrated half-cell). For the same reasons, measurements were carried out either one or a few times a day.

The heights of the solutions were always measured without the agitators. Apart from these brief instants for measurements, the agitators were always soaked in the solutions whose levels remained above the whole exposed membrane area. The conductivity and temperature of the solutions were measured with a conductivity meter (Eutech/Oakton CON 11, Singapore/United States of America) whose conductivity electrode was equipped with a built-in temperature sensor (EC-CONSEN91W 35608-50). Conductivities were converted to concentrations by means of calibration curves. We highlight that the conductivity measurements were performed systematically first in the dilute solution and only after in the concentrated compartment and that the electrode was always rinsed and wiped before and after each of these measurements.

A blank test was performed with pure distilled water at the same experimental conditions from the other experiments during 7.98 (rather hotter) days and resulted in 1 mm water loss by evaporation in each compartment, hence \( \sim 1.7\% \) of the initial volume. Loss of solution occurred essentially during the conductivity measurements when wiping the conductivity electrode after each measurement. The only exception was during the second experiment that started with a concentration difference of \( C_0^+ = 35 \text{ g L}^{-1} \) with the membrane BW30, when a higher volume of concentrated solution was lost through a leak in the concentrated compartment’s base.

The temperature of the solutions varied with the temperature in the room. The liquid levels were measured with a graduated ruler. The same membrane sample was used for all experiments with an specific membrane type; experiments with the same sample were carried out within some days interval during which it was immersed in 0.5 L pure distilled water.
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Figure 2.5: Schematic representation of the double stirred diffusion cell employed for the determination of the membrane permeability coefficients via osmosis and diffusion. On the left-hand side, the front view of one half-cell in the direction parallel to the membrane. On the right hand side, the front view of the entire experimental setup the direction perpendicular to the membrane position. Drawing in approximate scale.

Figure 2.6: Double stirred diffusion cell employed the determination of the membrane permeabilities.

(a) Start of an experiment with the diffusion apparatus. The lid houses the gear of the stirring system put in motion by the motor on the top. The colored wires are for the motor power supply.

(b) On the outer side of the compartments’s walls, the horizontal cylinder-shaped projection (left half-cell) and depression (right half-cell) between which the membrane is fastened.
2.2.4.2 Results and Discussions: Osmotic-Diffusive Experiments and Membrane Permeabilities

In order to test the hypothesis of concentration-dependent permeabilities and to quantify this dependence if applicable, we evaluated a wide range of sodium chloride concentrations representative of low-concentration brackish waters up to standard seawater and carried out our experiments at three initial concentrations $C_0$ in the concentrated compartment (or initial concentration differences $\Delta C_0$): $1 \text{ g} \cdot \text{L}^{-1}$, $10 \text{ g} \cdot \text{L}^{-1}$ and $35 \text{ g} \cdot \text{L}^{-1}$. For the sake of clarity, we present and discuss these values in the present section more concisely, but present in Figure 2.7, for illustration, one example. The complete results are in Appendix B.

Certain values of concentration of the concentrated solution randomly fluctuated sometimes, notably at high concentrations, and assumed incoherent values at these points (e.g. higher than the initial concentration or having a dissimilar trend from its previous and following values). These incongruities are exclusively due to unexpected bad functioning of the conductivity meter. For this reason, all the results in this thesis were calculated based on conductivity measurements performed in the dilute half-cell only (Equations 2.48, 2.63, 2.67, 2.68 and others).

We develop a rationale for, to some extent, considering estimates of solvent and solute leaks in the subsequent calculations.

Consider $\delta V_{\text{osm}}(t)$ the volume of solvent drawn until time $t$ from the dilute solution – the “solvent reservoir” – into the concentrated solution via osmosis and $\delta M_{\text{diff}}(t)$ the amount of solute which simultaneously diffused in the opposite direction (i.e., from the concentrated compartment – “solute reservoir”):

No expression is known neither for the volume loss, $\delta V_{\text{leak}}(t)$, nor for the solute loss, $\delta M_{\text{leak}}(t)$, in the dilute compartment (neither in the concentrated). Considering that water evaporation and that wiping of the conductivity electrode are virtually equivalent for both compartments, and by postulating that other leaks through contact points are equally distributed between the two sides, we could write:

$$\delta V_{\text{leak}}(t) = \frac{V_0^- + V_0^+ - V^-(t) - V^+(t)}{2} \quad (2.69)$$

The following approximation is done:

$$\delta M_{\text{leak}}(t) = [C^-(t) - C_0^-] \delta V_{\text{leak}}(t) \quad (2.70)$$
Figure 2.7: Experiments with the membrane BW30 starting with $C_0^+ = 10\text{ g·L}^{-1}$ and $C_0^- = 0$. These and other results are presented in Appendix B.
The latter formula is a conservative assumption for the mass leak. We could have used alternatively the mean concentration difference.

Following this rationale, the volume and the concentration of each compartment corrected for leak can be estimated (subscript $\ast$). In the dilute half-cell for instance:

\[
V^-_s(t) = V^-(t) + \delta V^-_{\text{leak}}(t) \tag{2.71}
\]
\[
C^-_s(t) = \frac{C^-(t)V^-(t) + \delta M^-_{\text{leak}}(t)}{V^-_s(t)} \tag{2.72}
\]

Plots of $\delta V_{\text{osm}}(t)/V^-_0$ ($V^-_0$ is practically the same for all experiments) and of $\delta M_{\text{diff}}(t)$ against the elapsed time facilitate the comparison between the experiments with different initial values and durations. The graphs are shown in Figure 2.8. For all experiments, $\delta V_{\text{osm}}(t)/V^-_0$ and $\delta M_{\text{diff}}(t)$ increased measurably within the few days the experiments lasted for. Both transfers increased with $\Delta C_0$, what was expected because the driving force is higher. $\delta V_{\text{osm}}(t)/V^-_0$ was higher with the BW30 whereas $\delta M_{\text{diff}}(t)$ with the NF270 for all $\Delta C_0$. More precisely, $\delta M_{\text{diff}}(t)$ varied notably little with time for the BW30; we could also say that it varied similarly little for the NF270 at the weakest driving force $\Delta C_0 = 1\,\text{g}\cdot\text{L}^{-1}$. In other words, the osmotic effect is stronger with the most selective membrane (the RO one), and the solute transfer is the most important one for the least selective one (the NF membrane). The total solute transfer proportional to the total amount of solute available at $t = 0$ in the concentrated solution, $\delta M_{\text{diff}}(t)/C^+_0V^+_0$, proved to increase in the opposed direction of $\Delta C_0$ as plotted in Figure 2.9. In fact, as we will soon verify, the salt permeabilities decreased with increasing concentration. Four experiments were repeated: BW30 at $\Delta C_0$ of 1 g·L$^{-1}$ and 35 g·L$^{-1}$ and NF270 at 1 g·L$^{-1}$ and 10 g·L$^{-1}$. The repeatability from the point of view of $\delta V_{\text{osm}}(t)/V^-_0$ and of $\delta M_{\text{diff}}(t)$ was bad for the BW30 at $\Delta C_0$ 1 g·L$^{-1}$ (water and salt), and passable for the salt with the NF270 at 10 g·L$^{-1}$. The variation of the temperature could in principle explain part of these deviations, but having not been tracked continuously along an experiment (only in the instant of the measurement), it is difficult to quantify it reliably.

In the following, the concentration and volume at each time $t$ assume the values $V^-_s(t)$ and $C^-_s(t)$ as in Equation 2.71 and Equation 2.72.

The solute permeability values have been determined by two methods. The first one is a “mixed” method. It consists in calculating the ratio $B/(I_0^{-1})^\dagger$ or $(I_0^{-1})^\dagger/B$ graphically by fitting experimental data to Equation 2.63, and then to obtain $B$ by
(a) Fraction of water of the dilute solution which permeated the membrane by osmosis within a given time.

(b) Mass of salt which diffused thorough the membrane within a given time.

Figure 2.8: Water and salt transferred from one solution to the other as a function of time.
considering (supposing) the water permeability value $I_0^{-1}$ determined previously in pressure-driven mode (Table 2.1). The corresponding plots are in Figure 2.10 and Figure 2.11. Table 4.6 summarizes the ratios $B/(I_0^{-1})^\dagger$ calculated for all experiments by the first method\textsuperscript{19}.

The second method enables to determine simultaneously the solute and the solvent permeabilities by fitting them numerically to Equations 2.67 and 2.68, that means, by using values obtained during osmotic-diffusive experiments only. The corresponding plots are shown in Figure 2.12 and the results grouped in Table 2.3. Notice that it is possible to calculate the ratio $B/(I_0^{-1})^\dagger$ by this second method too, once the individual permeabilities are determined. By comparing the Tables with the ratios obtained with both methods, it is seen that the methods give consistent results (as expected).

In Figures 2.10a, 2.12a and 2.13a (dilute compartment, experiment $n^\circ$ I with the BW30 membrane with $C_0^+ = 1 \text{ g} \cdot \text{L}^{-1}$), a discontinuity exists after the first measure-

\textsuperscript{19} Linear fitting weighted at each data point with the values of vertical error as explained in section ??.
The conductivities measured in this zone are the lowest of all experiments and did not differ much from the pure water conductivity. We interpret this discontinuity as being possibly due to a jump in the sensitivity of the conductivity meter at some point in this very dilute zone. During experiment \( n^\circ II \), measurements were carried out fewer times, so that discontinuity is less perceptible.

The order of magnitude of \( B/(I_0^{-1})^\dagger \) for the two membranes is totally different: \( \mathcal{O}(1 \text{ mol}\cdot\text{m}^{-3}) \) for the BW30 membrane and \( \mathcal{O}(10^4 \text{ mol}\cdot\text{m}^{-3}) \) up to \( \mathcal{O}(10^2 \text{ mol}\cdot\text{m}^{-3}) \) for the NF270. The table shows that the permeability ratio is sensibly dependent on the initial concentration difference. In rough terms, it has more than a twofold increase for the BW30 when the lowest initial concentration is multiplied by 10 and up to a threefold increase when it is multiplied by 35. For the NF270, the increase is of two to three times when passing from \( \Delta C_0=1 \text{ g}\cdot\text{L}^{-1} \) to \( \Delta C_0=10 \text{ g}\cdot\text{L}^{-1} \), and about sixfold at the highest initial concentration difference. Repeated measurements with the BW30 coincide at \( \Delta C_0=35 \text{ g}\cdot\text{L}^{-1} \) and differ (for the mean \( B/(I_0^{-1})^\dagger \)-values) of approximately 23\%–30\% at \( \Delta C_0=35 \text{ g}\cdot\text{L}^{-1} \) (values do not overlap in the confidence intervals); for the NF270, they differ of 9\% at \( \Delta C_0=1 \text{ g}\cdot\text{L}^{-1} \) (values overlap in the confidence intervals) and of 20\%–26\% at \( \Delta C_0=10 \text{ g}\cdot\text{L}^{-1} \) (values do not overlap in the confidence intervals).

We present now the results obtained with the second method (pure osmosis-diffusion). Initial values for the numerical identification of \( (I_0^{-1})^\dagger \) and \( B \) can be

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( C_0^+ (\text{g} \cdot \text{L}^{-1}) )</th>
<th>Test</th>
<th>( B/(I_0^{-1})^\dagger (\text{mol} \cdot \text{m}^{-3}) )</th>
<th>95% LCL</th>
<th>95% UCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW30</td>
<td>1</td>
<td>I</td>
<td>1.8</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1.8</td>
<td>1.7</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>I</td>
<td>3.8</td>
<td>3.7</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>4.0</td>
<td>3.8</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>5.2</td>
<td>4.8</td>
<td>5.6</td>
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<td>II</td>
<td>60.9</td>
<td>54.3</td>
<td>69.2</td>
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<td>10</td>
<td>I</td>
<td>66.3</td>
<td>57.8</td>
<td>77.9</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>137.3</td>
<td>124.7</td>
<td>152.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>173.1</td>
<td>160.0</td>
<td>188.5</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>381.7</td>
<td>356.3</td>
<td>411.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Ratio \( B/(I_0^{-1})^\dagger \) calculated by means of Equation 2.63 for all experiments. The mean value and the 95\% lower and upper confidence limits (LCL and UCL) are presented. The corresponding plots (with inverted axes) are shown in Figure 2.10 and Figure 2.11.
(a) BW30 with $C_0^+ = 1 \text{ g.L}^{-1}$, experiment n° I.

(b) BW30 with $C_0^+ = 1 \text{ g.L}^{-1}$, experiment n° II.

(c) BW30 with $C_0^+ = 10 \text{ g.L}^{-1}$.

(d) BW30 with $C_0^+ = 35 \text{ g.L}^{-1}$, experiment n° I.

(e) BW30 with $C_0^+ = 35 \text{ g.L}^{-1}$, experiment n° II.

Figure 2.10: By inverting Equation 2.63, the slope of the plots above gives the ratio $(I_0^{-1})^+ / B$ of different experiments with the BW30 membrane.
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(a) NF270 with $C_0^+ = 1 \text{ g} \cdot \text{L}^{-1}$, experiment $n^\circ$ I.

(b) NF270 with $C_0^+ = 1 \text{ g} \cdot \text{L}^{-1}$, experiment $n^\circ$ II.

(c) NF270 with $C_0^+ = 10 \text{ g} \cdot \text{L}^{-1}$, experiment $n^\circ$ I.

(d) NF270 with $C_0^+ = 10 \text{ g} \cdot \text{L}^{-1}$, experiment $n^\circ$ II.

(e) NF270 with $C_0^+ = 35 \text{ g} \cdot \text{L}^{-1}$.

Figure 2.11: By inverting Equation 2.63, the slope of the plots above gives the ratio $(I_0^{-1})^*/B$ of different experiments with the NF270 membrane.
guesstimated from the integration of experimental data of volume and concentration.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( C_0^+ ) (g·L(^{-1}))</th>
<th>Test</th>
<th>((I_0^-)^\dagger) (m(^4)·s(^{-1})·mol(^{-1}))</th>
<th>B (m·s(^{-1}))</th>
<th>( B/(I_0^-)^\dagger ) (mol·m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW30</td>
<td>1</td>
<td>I</td>
<td>3.2 × 10(^{-8})</td>
<td>5.6 × 10(^{-8})</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>9.0 × 10(^{-8})</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>I</td>
<td>1.0 × 10(^{-8})</td>
<td>3.6 × 10(^{-8})</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>3.6 × 10(^{-9})</td>
<td>1.9 × 10(^{-8})</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>3.4 × 10(^{-9})</td>
<td>1.5 × 10(^{-8})</td>
<td>4.4</td>
</tr>
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<td></td>
<td></td>
<td>II</td>
<td>3.6 × 10(^{-9})</td>
<td>1.9 × 10(^{-8})</td>
<td>5.3</td>
</tr>
<tr>
<td>NF270</td>
<td>1</td>
<td>I</td>
<td>7.3 × 10(^{-9})</td>
<td>4.6 × 10(^{-7})</td>
<td>62.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>7.3 × 10(^{-9})</td>
<td>4.4 × 10(^{-7})</td>
<td>60.2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>I</td>
<td>1.9 × 10(^{-9})</td>
<td>2.6 × 10(^{-7})</td>
<td>130.8</td>
</tr>
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<td></td>
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<td>2.2 × 10(^{-9})</td>
<td>3.8 × 10(^{-7})</td>
<td>173.3</td>
</tr>
<tr>
<td></td>
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<td>I</td>
<td>7.3 × 10(^{-10})</td>
<td>2.6 × 10(^{-7})</td>
<td>348.9</td>
</tr>
</tbody>
</table>

Table 2.3: Values of \((I_0^-)^\dagger\), B and \(B/(I_0^-)^\dagger\) determined by fitting the permeability coefficients to the numerical solution of the system composed of Equation 2.67 and Equation 2.68. The corresponding plots are shown in Figure 2.12.

Both \((I_0^-)^\dagger\) and B of the two membrane samples decreased significantly as the initial concentration difference was raised. The decrease was such for \((I_0^-)^\dagger\) that its magnitude decreased of one order from \(\Delta C_0=1\) g·L\(^{-1}\) to \(\Delta C_0=35\) g·L\(^{-1}\). From \(\Delta C_0=1\) g·L\(^{-1}\) to \(\Delta C_0=10\) g·L\(^{-1}\), the reduction was inferior, however still significant. The proportional reduction of B with \(\Delta C_0\) among all experiments with the membrane BW30 ranged between 1.5 and 6 times; it was not more than 1.8 times for the NF270. The decrease of the free volume in the polymer with consequent decrease of diffusion coefficients could be behind this behavior, as explained in section 2.1.3.1 (Equation 2.36).

From Table 2.3, we also verify that the salt permeability of the NF270 nanofiltration membrane is higher than the corresponding value of the BW30 reverse osmosis membrane of about one order of magnitude. Curiously, the (unanticipated) opposite applies for the water permeability: the NF270 was the less water-permeable of the two samples.

Some comments about the latter observation: (i) We have modeled the experiments with the solution-diffusion model, therefore neglecting any effect of Staverman’s reflection coefficient. In light of this second possibility, we would actually be determining \(\sigma(I_0^-)^\dagger\) instead of only \((I_0^-)^\dagger\). For the water permeabilities of the
CHAPTER 2. Membrane Transport

(a) BW30 with $C_0^+ = 1 \, \text{g·L}^{-1} = 17 \, \text{mol·m}^{-3}$.

(b) NF270 with $C_0^+ = 1 \, \text{g·L}^{-1} = 17 \, \text{mol·m}^{-3}$.

(c) BW30 with $C_0^+ = 10 \, \text{g·L}^{-1} = 171 \, \text{mol·m}^{-3}$.

(d) NF270 with $C_0^+ = 10 \, \text{g·L}^{-1} = 171 \, \text{mol·m}^{-3}$.

(e) BW30 with $C_0^+ = 35 \, \text{g·L}^{-1} = 599 \, \text{mol·m}^{-3}$.

(f) NF270 with $C_0^+ = 35 \, \text{g·L}^{-1} = 599 \, \text{mol·m}^{-3}$.

Figure 2.12: Plots of experimental results and numerical solutions of Equation 2.67 and Equation 2.68 with values of $(I_0^{-1})^\dagger$ and $B$ obtained by parametric fitting and listed in Table 2.3.
NF270 to be of the same order of those from the BW30, $\sigma$ would need to be of order $\mathcal{O}(10^{-1} - 10^{-2})$; these values seem too low if no pressure is applied, as is the case with the osmotic-diffusive experiments. (ii) The water and salt flowing in opposite directions within the membrane, diffusion-induced convection could be important. The NF270 gives lower water fluxes and higher salt fluxes compared to the BW30, so that this effect would be more pronounced within the NF270. (iii) Until now, we referred qualitatively to sorption and diffusion coefficients in order to understand permeability, and evoked that, because NF membranes would in general have less rigid, less cross-linked and more hydrophilic structures than RO membranes, membrane swelling in NF would be higher than in RO and so their respective water permeabilities (sections 2.1.3.1 and 2.2.3.2). The literature [Strathmann, 2011, p. 239] cites however that the water permeability can be low even if the water sorption is high in the case where water clusters are formed because the latter increase the activation energy for the water to diffuse across the membrane. This mechanism, if more pronounced with the NF270 than with the BW30, could perhaps underlie the behavior that we found for $I_{\theta}^{-1}$.

Still from Table 2.3, the values of ($I_{\theta}^{-1}$)$^\dagger$ were well repeatable for the BW30 at $\Delta C_0=35\text{ g}\cdot\text{L}^{-1}$ (deviation $< 6\%$), the NF270 at $\Delta C_0=1\text{ g}\cdot\text{L}^{-1}$ (identical) and for the NF270 at $\Delta C_0=10\text{ g}\cdot\text{L}^{-1}$ (deviation $< 16\%$). It was however bad for the BW30 at $\Delta C_0=1\text{ g}\cdot\text{L}^{-1}$ (deviation $> 35\%$). As for $B$, repeatability was mostly bad. For the BW30 at $\Delta C_0=1\text{ g}\cdot\text{L}^{-1}$, the deviations are $> 35\%$, about $25\%$ for the BW30 at $\Delta C_0=35\text{ g}\cdot\text{L}^{-1}$, and $> 30\%$ for the NF270 at $\Delta C_0=10\text{ g}\cdot\text{L}^{-1}$. Therefore, we cannot state that the measurements of $B$ are repeatable. No satisfactory explanation has been found for it. Finally, the comparison of experiments n$^o$ I and II for the BW30 at $\Delta C_0=1\text{ g}\cdot\text{L}^{-1}$ reveals, interestingly, that ($I_{\theta}^{-1}$)$^\dagger$ and $B$ varied of the same proportion, reason their $B/($($I_{\theta}^{-1}$)$^\dagger$ are identical, in spite of the fact that the experiments were not repeatable. If not fortuitous, this could perhaps indicate a similar behavior between the membrane’s properties that determine the water transfer and those accounting for the salt transport.

The comparison of Table 4.6 and Table 2.3 reveals good agreements between the results for $B/($($I_{\theta}^{-1}$)$^\dagger$ by the two methods. For very small deviations, the consideration of the confidence intervals in Table 4.6 did not render possible the overlapping of all values (more precisely, of BW30 at $\Delta C_0=1\text{ g}\cdot\text{L}^{-1}$ and of experiment n$^o$ I at $\Delta C_0=35\text{ g}\cdot\text{L}^{-1}$, and of NF270 at $\Delta C_0=35\text{ g}\cdot\text{L}^{-1}$).

The calculation of $B$ from $B/($($I_{\theta}^{-1}$)$^\dagger$ is obviously entirely dependent on the value of
previously determined, whatever were the means for this determination. In Table 2.4, the salt permeabilities determined by combining the values of $B/(I_0^{-1})$ from osmotic-diffusive experiments with the values of water permeability determined in pressure-driven mode during the membrane conditioning phase (Table 2.1) are presented. The salt permeabilities values thus determined are up to three orders of magnitude higher than their “homologs” not subject to an applied pressure.

Table 2.4 also presents results when Equation 2.48 (for no solvent flux) is used. Accordingly, $B$ is directly proportional to $V_0$, here set to $V_0^-$. A close agreement is verified between the salt permeabilities thus calculated and the “osmotic-diffusive” ones for the cases where the volume varied little, i.e. for the NF270. On the contrary, when the water osmotic flux is not negligible (experiments with the BW30), the differences range from 27% to 45% as a result of the variable slope of Equation 2.48. The corresponding plots are shown in Figure 2.13.

Finally, it is important to remind that a single sample of each membrane has been used for all experiments. As mentioned in section 2.1.3.3, it is not reliable to affirm a priori that the same permeability values would have been found with other samples. This only adds more difficulty to the task of scaling up membrane processes relying on data from test-cell experiments [Schipolowski et al., 2006].
Figure 2.13: Plots of experimental results under the form of Equation 2.48 which applies in principle for compartments with constant volume. The slopes contain the value of the solute permeability summarized in Table 2.4.
<table>
<thead>
<tr>
<th>Membrane</th>
<th>( C_0^+ ) (g·L(^{-1}))</th>
<th>Test</th>
<th>( I_0^{-1} ) (m·Pa(^{-1})·s(^{-1}))</th>
<th>( B ) (m·s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW30</td>
<td>1</td>
<td>I</td>
<td>6.5 × 10(^{-12})</td>
<td>8.7 × 10(^{-12})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>1.1 × 10(^{-11})</td>
<td>8.7 × 10(^{-12})</td>
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<tr>
<td></td>
<td>10</td>
<td>I</td>
<td>2.1 × 10(^{-12})</td>
<td>8.7 × 10(^{-12})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>7.0 × 10(^{-13})</td>
<td>8.7 × 10(^{-12})</td>
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<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>7.4 × 10(^{-13})</td>
<td>8.7 × 10(^{-12})</td>
</tr>
<tr>
<td>NF270</td>
<td>1</td>
<td>I</td>
<td>1.5 × 10(^{-12})</td>
<td>5.7 × 10(^{-11})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>1.5 × 10(^{-12})</td>
<td>5.7 × 10(^{-11})</td>
</tr>
<tr>
<td></td>
<td>10</td>
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<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>1.5 × 10(^{-13})</td>
<td>5.7 × 10(^{-11})</td>
</tr>
</tbody>
</table>

Table 2.4: Values of water permeability \( (I_0^{-1}) \) and sodium chloride permeability \( (B) \) summarized for all experiments with the RO membrane BW30 and NF membrane NF270 estimated by three different methods: independent determination of both coefficients by means of osmotic-diffusive experiments only (Osm.-diff.); mixed determination, whereby the osmotic-diffusive ratio \( B/(I_0^{-1}) \) is combined with the water permeability determined with pure water under pressure during the membrane conditioning phase (Mixed); determination of the salt permeability via the same osmotic-diffusive experiments but by setting \( V_0 = V_0^0 \) in the equation which assumes that no osmotic flux takes place (Pure diff.). From Equation 2.49, \( I_0^{-1} = (I_0^{-1}) \) \( / (iRT) \) with \( T = 293 \) K and \( i = 2 \).
2.3 Chapter Conclusion

A variety of transport mechanisms explain mass transfer across RO and NF membranes. Even though the theory of irreversible Thermodynamics provides a general background for these and other processes, the hypothesis of local equilibrium at the interfaces, the Onsager Reciprocal Relations and more generally the linear laws between fluxes and driving forces may not be always appropriate in membrane processes far from equilibrium. Hence, several models have been proposed over time and became classic in the membrane field (e.g. Kedem-Katchalsky and Spiegler-Kedem). By diversifying driving forces and by coupling fluxes, notably by considering convection as a transport mechanism, they should achieve better performances when describing solvent(s) and (specially) solute(s) fluxes, but on the other hand they require more transport parameters whose determinations are not straightforward and raise their own questions.

Fortunately, in water desalination with RO and tight-NF membranes, a simpler model reaches a good compromise between theory and praxis: the solution-diffusion model. It has the advantage of requiring only two transport parameters: the solvent (water) permeability and the solute (salt) permeability. Loose-NF membranes still cannot neglect the contribution of convection for the total mass transfer.

In this chapter, we proposed a method for the determination of the overall membrane permeability coefficients of the solution-diffusion model and, alternatively, of their ratio, by means of purely osmotic-diffusive experiments, i.e. when hydrodynamic pressure is not a driving force. Our method avoids two deleterious effects faced by customary approaches: in the case of pressure-driven processes, concentration polarization, and, in the case of applications driven by osmosis and solute diffusion, the neglect of the osmotic solvent flux. Using small amounts of solutions, employing few, simple experimental equipment and easy to implement and to operate, the method is advantageous from the operational point of view too.

Our second objective was to investigate whether the membrane’s state – i.e., its permeability coefficients – is dependent on the type and on the magnitude of the driving forces it is subject to and, if applicable, to quantify this influence.

Our results concerning the osmosis-driven permeation of water and the diffusion-driven permeation of sodium chloride between two compartments separated by the
RO membrane BW30 or by the loose-NF membrane NF270 confirmed the applicability and usefulness of our experimental protocol and of our method for the determination of permeability coefficients. The water permeabilities thus determined, when compared to water permeability values determined experimentally in a previous pressure-driven test, brought to light the inequivalence of the two coefficients by different orders of magnitude. This raises questions on the mechanisms of mass transfer actually engendered by the applied transmembrane pressure and by an “osmotic gradient” – i.e. solvent transmembrane activity gradient – and hence, by extension, on the term “osmotic pressure” in the context of membrane separations. The osmotic permeabilities proved to be strongly concentration-dependent. The corresponding salt permeabilities were also clearly dependent on the concentration gradient across the membranes, but to a lesser degree and within the same order of magnitude. Both decreased with increasing concentration, behaviors in qualitative accordance with transport theories. The experimental results confirmed that the osmotic flux has a central contribution in the evolution of the concentrations of solutions separated by a highly selective membranes, as indicated by the theory. In addition to this, we verified that the membrane conditioning protocol, notably the maximum conditioning pressure, plays an important role in the values of pressure-driven water permeability; we believe that this factor is determinant of the values obtained during osmosis-diffusion.

The adequacy of the coefficients determined herein, notably of the solute permeability, for the simulation of – pressure-driven – RO will be investigated and discussed in Chapter 4. The pertinence of the (not always optimal) repeatability of the permeability measurements verified in the previous pages will also be assessed from the point of view of their influences on the rejection rates and permeate fluxes. All this represents a third objective of the studies undertaken in the present Chapter.

Now, we have experimental results of mass transfer across membranes and saw that membrane transport is affected by the local conditions of concentration and of pressure on the interfaces of the membrane.

When implementing a separation process industrially with a RO membrane module, these local conditions are particularly dependent on the concentration polarization phenomenon, which results from the coupling between hydrodynamics and mass transfer in the feed channel of the module. The description of this coupling by means of a numerical model is the theme of the coming Chapter. The
experimental results obtained in the current Chapter will be revisited in the last Chapter.
CHAPTER 3

Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

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Membrane processes being largely affected not only by what takes place inside the membrane but also by the conditions in its vicinity, it is necessary to describe and to quantify the phenomena occurring in the module’s feed channel. Two phenomena are of special relevance: concentration polarization combined with osmosis and fouling. We proceeded in stages and opted to study concentration polarization in a first instance. This study is fundamentally different from the one of the previous chapter.
CHAPTER 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

The aim of the literature review is the modeling of concentration polarization in pressure-driven membrane processes in liquid phase. We introduce fundamental concepts of the field by presenting the basic models which describe the problem by means of averaged parameters only. Their limitations are pointed out and introduce the upper-level approaches leading to local models.

An extensive part of the chapter is dedicated to the set of progressive studies developed over the years in our research group on both purely hydrodynamic problems and problems coupling hydrodynamics to bulk solute transfer. This presentation has more than a historical interest. It contains an important number of definitions, concepts and results which we chose to introduce at the necessary time only. We felt it would be clearer to present them as we go along instead of all at once, in which case they would perhaps seem nebulous and surely dislocated. It starts with analytical studies and continues with the succeeding numerical model developed further and employed throughout this thesis.

Afterwards, we focus on those boundary conditions particularly relevant to transmembrane mass transfer and use the numerical model to simulate the extensive and interesting influence they have on diverse parameters of the whole problem.

Concluding remarks end the chapter.
3.1 Literature Review

3.1.1 Concentration Polarization

The solute or particle concentration precisely at the membrane surface determines the course and the outputs of several barometric membrane separations of which reverse osmosis and nanofiltration. Its value is the maximal magnitude of the solute concentration profile, or concentration polarization layer, which grows in the feed channel of the membrane module\(^1\) from the middle of the bulk solution toward the membrane as a result of the coupling of momentum and mass transfers, in turn dependent on the membrane properties (permeability). The modeling of this phenomenon is a point of convergence of membrane processes like reverse osmosis, nanofiltration, ultrafiltration and microfiltration and a necessary step in predicting their results.

When solution permeates through the membrane, solutes are rejected at the feed surface as a consequence of the membrane permselectivity. This naturally leads to a reversible\(^2\) buildup of retained solutes in this zone or, conversely, to a depletion in permeating solvents. A concentration gradient normal to the membrane appears between the membrane surface and the bulk, just as the corresponding net diffusive flow of solute oriented toward the bulk. This is called concentration polarization (CP). The magnitude of CP is frequently expressed by the concentration polarization modulus \(\Gamma_{mb}\) as the ratio of the concentrations of solute \(i\) at the membrane surface and in the bulk, \(C_m\) and \(C_b\):

\[
\Gamma_{mb} = \frac{C_m}{C_b} \tag{3.1}
\]

Concentration polarization moduli can also be defined in relation to the feed concentration. Typical orders of magnitude of \(\Gamma_{mb}\) in RO desalination are below 1.5 and about 70 in UF protein separation [Baker, 2004, p. 70]. The difference stems from the higher permeation rates and lower solute diffusion coefficients in UF.

Concentration polarization limits process performance significantly and, were not for technical solutions, its effects would be even more severe. The enhanced surface concentration increases the osmotic pressure difference across the membrane and reduces the permeate flux. At the same time, this higher solute transmembrane

---

\(^1\) Phenomenon much less pronounced on the filtrate side [Drioli and Giorno, 2010, p. 19].

\(^2\) Existing as long as the process’ driving force is applied (here, pressure).
concentration gradient raises the solute flux. Together, the two effects reduce the rejection rate\(^3\). Moreover, it causes the precipitation of solution’s components if their solubility limit is attained and accelerates fouling [Mulder, 1996, pp. 417–418; Strathmann, 2011, pp. 342–343; Baker, 2004, p. 241; Sablani et al., 2001].

In the next pages, we treat cross-flow only (or tangential flow filtration), the standard filtration mode in RO and NF. In this configuration, concentration polarization eventually reaches the steady state, in contrast to dead-end (or frontal) filtration, where the exit for the concentrate stream is absent and in which case the growth of the layer of accumulated solutes is continuous [Zeman and Zydney, 1996, p. 352; Fernández-Sempere et al., 2008]. We present different ways the cross-flow filtration has been approached and the coupling between hydrodynamics and solute mass transfer in the bulk solution has been modeled.

### 3.1.2 Averaged Models

A first approach consists in looking at the parameters of the problem as being constant along the flow length. Even if averaged values are not always representative of the real physics of a particular application, the literature shows that they work well on a case-by-case basis. At the same time, they shed light on important phenomena occurring in pressure-driven membrane separations. In the following, we present some of the most representative models of this category.

#### 3.1.2.1 Boundary Layer Film Model

The very popular boundary layer film model in fully developed flow implicates the existence of a mass transfer resistance in the vicinity of the membrane where it assumes the mass transport parallel to the membrane to be negligible. In this one-dimensional problem, the solute convected onto the membrane surface by the transverse fluid flow is balanced\(^4\) in steady state by the retro-diffusion of solute into the bulk and, if taken into account, by the transmembrane solute flow. This balance originates an unstirred, stagnant concentration boundary layer over the membrane [Strathmann, 2011, pp. 343–345]. Let \(C\) be the solute concentration, \(C_b\)

\(^3\) Concentration polarization with mixtures of macromolecular solutes can give rise to “dynamic” layers of different selectivity which can reject solutes of different molecular weight differently and ameliorate the rejection of some of them [Mulder, 1996, p. 420].

\(^4\) Solute transport by convection and by diffusion in the axial direction are not considered, neither pressure drop.
CHAPTER 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

Figure 3.1: Sketch of a cross-flow filtration process according to the boundary layer film model. The tangential flow is neglected in the concentration boundary layer spanning a short distance normal to the membrane (x-direction) and the problem is one-dimensional. Fluxes are indicated by the letter $J$ and the solute concentration by $C_s$. Subscripts $s$ and $v$ and superscripts $p$, $b$ and $w$ denote volume, solute, permeate, bulk and upstream surface respectively; convective and diffusive fluxes respectively are indicated by subscripts $\text{con}$ and $\text{diff}$. Figure adapted from Strathmann [2011, p. 344].

its concentration in the bulk, $C_m$ at the membrane surface and $C_p$ in the permeate. The volumetric permeate flux is $J_v$. The diffusion coefficient of the solute in the boundary layer solution is $D_{sb}$ and the concentration boundary layer thickness is $\delta$. The solute mass balance in a differential element of the film reads:

$$J_v C = D_{sb} \frac{dC}{dx} + J_v C_p \tag{3.2}$$

Integration from $x = 0$ (feed-side membrane surface) up to $x = \delta$ and from $C = C_b$ up to $C = C_m$ with constant $D_{sb}$ and the approximation that $J_v$ is constant in the film\(^5\) yields the general expression for the permeate flux according to the boundary layer film model:

$$J_v = \frac{D_{sb}}{\delta} \ln \left( \frac{C_m - C_p}{C_b - C_p} \right) \tag{3.3}$$

In the hypothesis of total rejection, $C_p = 0$ and the expression is simplified:

$$J_v = \frac{D_{sb}}{\delta} \ln \left( \frac{C_m}{C_b} \right) \tag{3.4}$$

Note that the dimensionless group $J_v \delta / D_{sb}$ has the form of a Péclet number ($Pe$). The ratio $D_{sb} / \delta$ is frequently treated as a unique entity and assimilated to a mass transfer coefficient, usually unknown, here denoted $k_{sb}$. Its calculation is discussed

\(^5\) A transverse profile would be more representative of the velocity normal to the membrane. In fact, the velocity of permeation $J_v$ is its value on the membrane surface only.
in the next section. It is, together with the difficult measurement of $C_m$, an important limitation of the film model.

### 3.1.2.1.1 Mass Transfer Correlations

Empirical correlations are called on for the calculation of $k_{sb}$. The mass transfer coefficient appears in the expression of the Sherwood number, $Sh$, which is function of the axial Reynolds number $Re$ and of the Schmidt number $Sc$:

\[
Sh = \frac{k_{sb}d_h}{D_{sb}} \quad (3.5)
\]

\[
Re = \frac{\rho W d_h}{\mu} \quad (3.6)
\]

\[
Sc = \frac{\mu}{\rho D_{sb}} \quad (3.7)
\]

In these equations, $d_h$ is a characteristic dimension, usually the hydraulic diameter, $\rho$ and $\mu$ are the fluid density and dynamic viscosity and $W$ is the axial velocity of the fluid.

The correlations have often the form $Sh = K' Re^a Sc^b$ or $Sh = K' Re^a Sc^b (d_h/L)^c$, where $K'$, $a$, $b$ and $c$ are adjustable parameters and $L$ the length of the flow channel. The use of correction factors for accounting for deviating behaviors is very common. These correlations have a definite range of applicability because they depend appreciably on many factors: module geometry and specificities; experimental conditions, especially the flow regime and the feed velocity (more generally, the $Re$ number); the range of $Sc$ etc.

It is judicious to mention that the permeation/suction enhances $k_{sb}$, making therefore the use of correlations borrowed from flows in non-porous channels doubtful. Indeed, suction thins the momentum boundary layer accentuating the axial velocity gradient, diminishing turbulence near the membrane surface and pushing the laminar-turbulent transition to $Re \sim 4000$ [Belfort and Nagata, 1985; Gekas and Hallström, 1987; Geraldes and Afonso, 2006; van den Berg et al., 1989; Velikovska et al., 2004]. Correlations which do not consider solute diffusion (caused by CP) are also questioned [Sablani et al., 2001]. Still, the exchange of correlations among membrane processes is not without risk, for the Schmidt numbers can be drastically different (typically 600 in RO and more than 10 000 in UF for example) [van den Berg et al., 1989]. Finally, correlations which do not account for the spatial variation of properties like viscosity and solute diffusion coefficient
can generate misleading conclusions [Gekas and Hallström, 1987].

A variety of correlations and correction factors being proposed in the literature (for instance in Gekas and Hallström [1987] and Geraldes and Afonso [2006]), the choice of the suitable one for a particular application is not always self-evident.

### 3.1.2.2 Gel Layer Model

The gel (or cake) layer model concerns, in practical terms, UF and MF above all else, for it contributes to the understanding of the limiting permeate flux behavior of these processes. The model considers that a gel layer is formed on the membrane surface when the concentration at this point exceeds a critical value \( C_g \).

The resistance of this new layer increases with the applied pressure, resulting in that the volumetric permeate flux remains constant at \( J_{v,\text{lim,gel}} \) [Strathmann, 2011, sec. 5.3.1.6]; osmotic effects are not included in the model’s primary formulation. Its mathematical expression for full rejection is actually based on the film model:

\[
J_{v,\text{lim,gel}} = k_{sb} \ln \left( \frac{C_g}{C_b} \right)
\]  

(3.8)

Observations that actual values of surface concentration vary with the feed velocity and bulk concentration, e.g. in Paris et al. [2002], indicate that, frequently the gel layer corresponds more to a very concentrated liquid layer than to a “true” gel unaffected by operating conditions. Indeed, the dependence of the thickness and of the surface concentration of the gel layer on the hydrodynamic conditions in cross-flow filtration, as well as their axial non-uniformity (both dependences are linked) is accepted [Sablani et al., 2001]. Besides, although certain compounds gel easily, as is the case with proteins, many macromolecular compounds (dextranes, for instance) do not evolve into gel form even at very high concentrations [Mulder, 1996, p. 431].

### 3.1.2.3 Osmotic Pressure Model

The basic idea of the osmotic pressure model is that the presence of solute in the fluid reduces the permeation by originating an osmotic pressure difference \( \Delta \pi \) across the membrane so that the effective pressure difference across it differs from
the applied transmembrane pressure difference $\Delta P$. The same idea is present in the membrane transport models examined in Chapter 2. The mass transfer resistance $R_m$ of the membrane itself is introduced explicitly. Because the osmotic pressure is determined by the surface concentrations, if the concentration gradient in the membrane vicinity is considerable, its value impact the magnitude of $\Delta \pi$. Mathematically, the model expresses the volumetric permeate flux as:

$$J_v = \frac{\Delta P - \Delta \pi}{\mu R_m}$$

(3.9)

The occurrence of a limiting permeate flux value may be interpreted in the light of this approach [Mulder, 1996, sec. VII.7.].

The calculation and experimental measurement of osmotic pressures is a scientific subject in itself. Generically understood as being a colligative property, they are higher for low molecular weight solutes than for macromolecules at same mass concentration. In membrane separations however, high permeate fluxes combined with high rejections and low bulk mass transfer coefficients can lead to significant osmotic pressures even for macromolecules.

The classic van’t Hoff equation is frequently used for the calculation of $\pi$ or $\Delta \pi$. It has the same form of the ideal gas law, relating the osmotic pressure linearly to the absolute temperature $T$ and molarity $C$ of the solution by means of the coefficient $i$, so-called van’t Hoff factor corresponding to the number of dissociated entities (ionic or neutral) per “molecule” of solute in solution, and of the universal gas constant $R$:

$$\pi = iRTC$$

(3.10)

The relation is verified for “extremely dilute” solutions [Yokozeki, 2006] but is known not to hold even for very diluted solutions (e.g. bovine serum albumin, polyethylene glycol, hemoglobin), even though there is no prefixed limit for the concentration value, the applicability of the theory needing to be assessed empirically [Grattoni et al., 2007]. A “largely forgotten” improvement over this relation was given by Morse who proposed to replace molarity for molality [Wilson and Stewart, 2013]. In reality, the expansion of the osmotic pressure in series of the concentration value (up to the quadratic term generally) is more appropriate for reproducing experimental data for “general dilute solutions” [Yokozeki, 2006]. Thermodynamic modeling based on experimental data and activity models

---

7 A parallel should be drawn with the solvent permeability of the previous chapter.
Chapter 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

It is nowadays common for the prediction of $\pi$ at different conditions of temperature and concentration [Wilson and Stewart, 2013].

Table 3.1 illustrates for several aqueous solutions to which extent the osmotic pressure values can deviate from van’t Hoff’s osmotic pressure law, specially at high concentrations.

<table>
<thead>
<tr>
<th>Solute mass fraction (%)</th>
<th>$\pi_{vH}/\pi_{alt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
</tr>
<tr>
<td>0.05</td>
<td>0.953</td>
</tr>
<tr>
<td>0.5</td>
<td>0.950</td>
</tr>
<tr>
<td>5</td>
<td>0.921</td>
</tr>
<tr>
<td>9</td>
<td>0.897</td>
</tr>
</tbody>
</table>

Table 3.1: Ratio of the osmotic pressure values calculated for aqueous solutions of different solutes and concentrations using van’t Hoff’s osmotic pressure law (Equation 3.10), $\pi_{vH}$, and alternative expressions, $\pi_{alt}$, from Geraldes et al. [2002].

For NaCl, $\pi_{alt} = 805.1 \times 10^5 \omega$. For Na$_2$SO$_4$, $\pi_{alt} = 337.8 \times 10^5 \omega^{0.95}$. For sucrose, $\pi_{alt} = 72.18 \times 10^5 (\omega + 0.94\omega^2 + 2.93\omega^3)$. For PEG1000, polyethylene glycol of 1000 g·mol$^{-1}$, $\pi_{alt} = 24.64 \times 10^5 (\omega + 2.94\omega^2 + 19.25\omega^3)$. Values of $\pi_{alt}$ given in Pa; $\omega$ is the solute mass fraction comprised between 0 to 1.

Given the substantial variations, the choice of the most convenient osmotic pressure law is an important step in the quantitative modeling of membrane separations.

### 3.1.2.4 Resistance-in-Series Model

The well-known concept of additive transfer resistances from Transport Phenomena is applied to membrane separations by the resistance-in-series model. As illustrated in Figure 3.2, the resistances appearing in the previous models can be summed, the expression remaining open to be incremented of resistances corresponding to other phenomena [Cheryan, 1998, pp. 132–134]:

$$J_v = \frac{\Delta P}{\mu(R_m + R_{CP} + R_g + R_{foul} + ...)}$$  \hspace{1cm} (3.11)

The denominator contains $R_m$, $R_{CP}$, $R_g$ and $R_{foul}$ are the mass transfer resistances represented by the membrane itself and by the polarization, gel and fouling layers respectively. The osmotic pressure could have been included in the numerator as done in Equation 3.9.
CHAPTER 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

Figure 3.2: Illustration of the concept of additive mass transfer resistances in membrane filtration according to the resistance-in-series model. Figure from Mulder [1996, p. 417].

The models above were presented in an isolated manner, but this obviously does not represent the physical reality of most processes. Therefore, it is common practice to combine the different approaches in unified treatments more characteristic of each study.

Remains the difficulty of unraveling all these terms (polarization, gel, fouling, osmotic counter-effect), either experimentally or mathematically, even more when a complex solution is treated or when the filtration module has an intricate structure (designed to reduce these resistances!). Whatever the case may be, it is reasonable to expect that the limits of these phenomena be unclear and that their effects on the process behavior be not totally distinguishable. The variability according to hydrodynamic conditions and spatial position do not make the task easier. The averaged models can be satisfactorily employed on a case-by-case basis, but lacks generality.

It is worth noting that these models are built around the calculation of the filtrate throughput independently of that of its concentration. Needless to say, the latter field is matter of other kind of models discussed in the previous Chapter. If, however, the task of describing or of predicting process outputs globally is understood as also encompassing the determination of the filtrate concentration, the effectiveness of the present models, when combined to membrane transport models, is still to be established.

All this directs attention to modeling approaches which attempt to account for these phenomena on a local level by starting from the description of the more fundamental physics of the problem. The rest of this Chapter is seen through these lenses.
3.1.3 Local Models

An alternative approach to averaged phenomenological models is founded upon the fact that, fundamentally, all parameters of the membrane separation problem evolve locally in all directions. Local models propose to calculate the value of each variable, e.g. concentration, pressure and velocity, at any point in the domain of interest most frequently by solving the general transport equations for fluids and solutes simultaneously and under applicable boundary conditions. Depending on the problem to be treated and on the level of assumptions, analytical or numerical solutions are employed. In-house codes or simulation packages may be used. The more complex formulation and resolution of the problem should be compensated by clear gains in comprehensiveness, accuracy and predictability. The literature on such models is substantial; the examples we cite below, qualitatively only, are surely not exhaustive.

A review of models is presented in Bernales [2013]; Bernales et al. and mentions a great diversity of approaches. The pressure drop along the flow channel is illustrative of it: on the one hand it is neglected in some approaches\(^8\); on the other hand, it has been calculated by others by means of standard relations which are very different conceptually, like Ergun’s or Hagen-Poiseuille’s equations. Instead of a two-dimensional conception of the problem, a mathematical treatment might be employed according to which integration is carried out in the axial direction only, thereby amounting to a somewhat film-type formulation in the direction normal to the membrane. The axial velocity profile is also a point of contrast: plug flow, parabola, linearity. The concentration polarization layer may or not be considered to span the whole channel height... An example of approach which do not resort to the transport equations is that from Roth et al. [2000]. The model is analogous to a plug flow with dispersion and considers the feed channel of a spacer-filled\(^9\) module as a sequence of perfect mixing cells whose boundaries (the membranes) are dead-end zones to where a constituent (e.g. a tracer component) can migrate.

The assumption of negligible longitudinal variation of the cross-flow rate and of the axial velocity in view of the very low volume recoveries by permeation has already been adopted [Paris et al., 2002]. Differently, uniformity of concentration and of axial velocity at each transverse cross-section might be chosen Zhou et al. [2006].

\(^8\) The importance of the longitudinal evolution of the pressure in the flow channel, specially for long ducts, will be discussed in section 3.2.1.2.

\(^9\) More details on spacer-filled modules in section 4.2.
The polarization layer may also be assumed to have predetermined forms: its thickness can have for instance either a power-wise dependence upon the transverse direction or a dependence on the cube root of the distance from the entrance of the feed channel [Belfort and Nagata, 1985; Kim, 2007]. Another case is that the solute concentration in excess of the feed concentration may be adopted in the mathematical formulation: the rationale behind this choice is that only the solute corresponding to this excess could be treated as stagnant [Zhou et al., 2006], the condition of stagnancy being actually implied and required when the solute mass balance on the membrane surface is written under the consideration of zero axial velocity (the most common case).

Finally, computational fluid dynamics (CFD) methods combined with mass transfer modeling is a frequent preference, all the more so as intricate membrane modules and flows are common and simulation softwares become widespread [Ahmad and Lau, 2007; Fletcher and Wiley, 2004; Geraldes et al., 2002; Ghidossi et al., 2006; Schwinge et al., 2004].

The rest of this chapter is devoted to the alternative approach and models developed in our research group over many years as well as to the adaptations incorporated in them within the scope of this thesis.

### 3.2 Our Approach

The literature reviewed in this section comprises initial studies which backgrounded our research group’s works, the novel analytical approaches proposed for determined hydrodynamic problems and their combination with solute mass transfer in the bulk solution. From there on, we enter in the less restrictive numerical approach and examine the numerical model which couples hydrodynamics, bulk mass transfer and transmembrane solute transfer. For the benefit of clarity, whenever possible, we organized this section so as to present concepts, notations and conclusions step-by-step in a cumulative stream of intricacy.

The increasing levels of complexity when modeling a membrane separation process as they have been assessed are explained in Figure 3.3.
Figure 3.3: Schematization of the progressive and unified approach developed in the research group for modeling pressure-driven membrane processes in liquid phase. The literature on uniform, $z$-independent liquid permeation has been revisited. Then, the flow of pure solvent between leaking walls has been developed for the case were it depends on the local transmembrane pressure. Afterwards, solutions (solvent with solute) started to be considered in the case of membranes impermeable to the solutes (total rejection) – therefore, the problematics of concentration polarization (uniform and locally-varying) and of osmosis have been introduced. Currently, the membrane is considered to reject solute partially, so that mechanisms of transmembrane solute transport are added to the model, and the mechanism of solvent permeation is modified. Analytical or numerical treatments have been preferred depending on the situation. Numerical and experimental validations have also been carried out at different stages.

### 3.2.1 Analytical Modeling of Hydrodynamics

In this part, problems on the flow of a pure liquid (“solvent”) are examined.

#### 3.2.1.1 Berman and Green Flows: Points of Departure

The background for the cross-flow models presented in the rest of this section is the exact solution developed by Berman [1953] to the Navier-Stokes equations for the steady, incompressible, laminar flow of a pure fluid with constant properties in
a symmetric, slit-type, two-dimensional\textsuperscript{10} duct of rectangular cross-section through whose equally permeable walls fluid is being withdrawn. The velocity of the fluid permeating the walls, $U_W$, is imposed uniform at all axial positions. In other words, the cross-flow is pressure-independent\textsuperscript{11}. A literature summary presented by Belfort and Nagata [1985] cites a personal communication of Green [1980] on the flow along a slit where suction takes place at one wall only (a plate-and-frame membrane module for example). We refer to this problem, which bears physical and mathematical similarity to Berman flow, as “Green flow”. Both cases are sketched in Figure 3.4 and recapitulated here.

The problems are characterized in dimensional form by the transverse and axial coordinates, $X$ and $Z$, by the unknown velocity field $\mathbf{V} = \{U, W\}$ (in the transverse and axial direction, respectively) and by the pressure $P$. The pressure on the filtrate side of the membrane is the reference pressure, set to zero. Subscript \textit{in} stands for values took at the channel entrance, subscript 0 for uniform values (hence, keeping the same value as at the entrance).

In the conditions enounced in the first paragraph, neglecting the gravity’s effect and other external forces and noting $\mu_0$ and $\rho_0$ the fluid’s dynamic viscosity and density, the problem in the domains $\Omega = \{-d < X < d\} \times \{0 < Z < L\}$ (symmetric channel) and $\Omega = \{0 < X < d\} \times \{0 < Z < L\}$ (asymmetric channel) is governed by the Navier-Stokes equations – continuity equation and momentum balance:

\begin{align}
\nabla \cdot \mathbf{V} &= 0 \quad (3.12) \\
\rho_0 (\mathbf{V} \cdot \nabla) \mathbf{V} &= -\nabla P + \mu_0 \Delta \mathbf{V} \quad (3.13)
\end{align}

Some brief definitions need to be presented at this point. Berman [1953] defined a Reynolds number with respect to the permeate flux (or filtration velocity), $U_W$, therefore characteristic of the flow in the transverse direction. We call it here $Re'$:

$$Re' \equiv \frac{\rho_0 U_W d}{\mu_0} \quad (3.14)$$

We shall introduce part of the nondimensionalization proposed by Haldenwang

\textsuperscript{10} Channel length much bigger than the distance between the walls, as considered throughout this thesis.

\textsuperscript{11} This hypothesis will be relaxed in the next section.
CHAPTER 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

(a) Berman flow takes place along a symmetric flow channel limited by two equally permeable walls where permeation is pressure-independent and axially uniform. The parameter $d$ is the channel half-height. The origin of the coordinate system is situated in the middle of the channel.

(b) Green flow occurs in an asymmetric flow channel with one permeable wall only where the fluid is subject to pressure-independent, axially uniform efflux. The parameter $d$ is the channel full-height. The origin of the coordinate system is situated on the impermeable wall.

Figure 3.4: Sketches of Berman and Green flows of a pure fluid. Permeation $U_W$ is axially uniform in both cases. Berman flow is axially symmetric, in contrast to Green flow. Drawing not to scale ($d \ll L$).

[2007], in light of which we examine Berman’s, Green’s and other works.\(^{12}\)

\[ x = \frac{X}{d} \quad z = \frac{Z}{L_{de}} \quad u = \frac{U}{U_W} \quad w = \frac{W}{W_{in}} \quad p = \frac{P}{P_{in}} \quad (3.15) \]

$L_{de}$ is the dead-end length or locus in the axial direction where the pure solvent would be exhausted (if in isobaric flow).\(^{13}\):

\[ L_{de} = \frac{W_{in}d}{U_W} \quad (3.16) \]

Over half the symmetric channel in Figure 3.4a, the following boundary conditions are considered: the transverse velocity equals the permeation flux on the permeable wall and is zero due to symmetry in the center of the symmetric channel. The axial velocity is zero on all walls (no-slip condition).\(^{14}\). Due to symmetry about a

\(^{12}\) In Haldenwang [2007], $u$ has another definition. This will be explained later on.

\(^{13}\) In Haldenwang [2007], $L_{de}$ has another definition. This will be explained later on.

\(^{14}\) In principle, we could call into question the adherence condition at impermeable surfaces and think of a non-zero slip velocity at the surface of a membrane, in which case a boundary
plane midway the walls, its derivative with respect to the transverse direction is
set to zero in Berman flow at this point.

\[ u(1, z) = 1 \quad u(0, z) = 0 \quad w(1, z) = 0 \quad \frac{\partial w}{\partial x}(0, z) = 0 \]

Berman looked for a solution to the Navier-Stokes equations over half the symmet-
ric channel by introducing a stream function \( \Psi_B(x, z) \) of the so-called [Haldenwang et al., 2010] Berman function, \( B(x) \), together with boundary conditions:

\[ \Psi_B(x, z) = (1 - z)B(x) \quad (3.17) \]
\[ u(x, z) \equiv -\frac{\partial \Psi_B}{\partial z} = B(x) \quad w(x, z) \equiv \frac{\partial \Psi_B}{\partial x} = (1 - z)B'(x) \quad (3.18) \]
\[ B(1) = 1 \quad B(0) = 0 \quad B'(1) = 0 \quad B''(0) = 0 \quad (3.19) \]

Substitution into the two-dimensional Navier-Stokes equations (Equation 3.13)
leads to a third-order non-linear ordinary differential equation [Berman, 1953;
Haldenwang, 2007] of \( B(x) \) (see below) and the so-called [Haldenwang, 2007] Berman’s constant \( K(Re^t) \).

\[ Re^t[B(x)B''(x) - B'(x)^2] - B'''(x) = K(Re^t) \quad (3.20) \]

Simulating the case of a flow confined between non-leaking walls, whose reso-
lution leads to the fundamental Hagen-Poiseuille flow in a rectangular channel,
this equation has a simpler form, \( B''(x) = K(Re^t) \), in the limit case of \( Re^t \rightarrow 0 \).

Conceiving thereby the effects of the permeable walls as being deviations from this
more basic problem, Berman decided on looking for a solution to the eponymous
flow in the form of a perturbation series with \( Re^t \) as the perturbation parame-
ter [Berman, 1953]. The solution is unique for \( Re^t \leq 12.165 \) [Haldenwang, 2007].

layer within the material can be significant as is often the case for porous mediums [Beavers and
Joseph, 1967; Saffman, 1971] but seldom mentioned in the membrane literature (two exceptions
are Belfort and Nagata [1985] and Kim [2007]). This “alternative” boundary condition would
alter not only the hydrodynamic problem but also the solute mass transfer in the channel since
the solute mass balance on the membrane surface would include the convective solute transfer in
addition to the diffusive transport normal to the membrane. Slip velocities have been calculated
and shown to be very small in RO (\( \sim 10^{-5} \text{ m s}^{-1} \)) and in UF and MF (\( \sim 10^{-4} \text{ m s}^{-1} \)) [Belfort and
Nagata, 1985], even more when compared to typical feed velocities (\( \sim 10^{-2} \text{ m s}^{-1} - 10^{-1} \text{ m s}^{-1} \)
in RO for example). In our view, given the very low permeabilities of the membranes and the
permeation mechanisms seen in the previous chapter, it is not realistic to compare membranes to
truly porous materials. As a matter of fact, the no-slip condition is questionlessly and successfully
adopted in the membrane field.
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From Haldenwang [2007]:

\[ B(x) \equiv \sum_{n=0}^{\infty} \frac{1}{n!} f_n(x) (Re^t)^n \quad K(Re^t) = \sum_{n=0}^{\infty} \frac{1}{n!} k_n (Re^t)^n \]  

(3.21)

Truncation at second order results in:

\[ f_0 = \frac{3x}{2} \left( 1 - \frac{x^2}{3} \right) \quad k_0 = 3 \]  

(3.22)

\[ f_1 = \frac{x}{280} (-2 + 3x^2 - x^6) \quad k_1 = -\frac{81}{35} \]  

(3.23)

\[ f_2 = \frac{3x}{140} \left( -\frac{703}{13860} + \frac{73x^2}{1155} + \frac{x^6}{70} - \frac{x^8}{36} + \frac{x^{10}}{990} \right) \quad k_2 = \frac{468}{13475} \]  

(3.24)

First-order expressions for the velocities and for the pressure in all points of the channel as functions of the channel dimensions, the fluid properties and the inlet conditions were derived [Berman, 1953]. In addition to these equations, other important facts drawn by Berman [1953] deserve to be highlighted:

- The permeation causes the axial velocity profile to be flatter at the center and steeper near the porous walls compared to Hagen-Poiseuilles’ parabolic profile, the deviations varying with the permeation rate;
- The axial pressure drop when permeation takes place is considerably less than in ducts with impermeable walls;
- A Berman-type profile develops soon along the channel if \( Re^t \leq 4 \) even if parabolic inlet conditions are applied; in filtration, typically, \( Re^t \leq \mathcal{O}(1) \) [Haldenwang, 2007].

An analogous mathematical treatment was applied by Bernales [2013] to Green flow. He considered the following boundary conditions:

\[ u(1, z) = 1 \quad u(0, z) = 0 \quad w(1, z) = 0 \quad w(0, z) = 0 \]

In this case, \( G(x) \) (see below), there called Green function, and a stream function \( \Psi_G(x, z) \) were used. Note that, as seen in Figure 3.4b, the coordinate system and the definition of \( d \) changes and, with it, those of the dimensionless numbers it is
part of \((Re^t, L_{de}, x, z)\), as well as the interpretations of some boundary conditions.

\[
\Psi_G(x, z) = (1 - z)G(x) \tag{3.25}
\]

\[
u(x, z) \equiv -\frac{\partial \Psi_G}{\partial z} = G(x) \quad w(x, z) \equiv \frac{\partial \Psi_G}{\partial x} = (1 - z)G'(x) \tag{3.26}
\]

\[
G(1) = 1 \quad G(0) = 0 \quad G'(1) = 0 \quad G'(0) = 0 \tag{3.27}
\]

Also:

\[
Re^t[G(x)G''(x) - G'(x)^2] - G'''(x) = K(Re^t) \tag{3.28}
\]

Similarly:

\[
G(x) \equiv \sum_{n=0}^{n=\infty} \frac{1}{n!} f_n(x) (Re^t)^n \quad K(Re^t) = \sum_{n=0}^{n=\infty} \frac{1}{n!} k_n (Re^t)^n \tag{3.29}
\]

At second order:

\[
f_0 = 3x^2 - 2x^3 \quad k_0 = 12 \tag{3.30}
\]

\[
f_1 = -8x^2 + 27x^3 + 3x^5 - \frac{2x^7}{5} - \frac{35}{35} \quad k_1 = -\frac{81}{35} \tag{3.31}
\]

\[
f_2 = -\frac{761x^2}{323400} - \frac{2929x^3}{161700} + \frac{16x^5}{175} - \frac{113x^6}{1050} + \frac{54x^7}{1225} - \frac{3x^8}{280} + \frac{x^9}{105} - \frac{4x^{10}}{525} + \frac{8x^{11}}{5775} \quad k_2 = \frac{2929}{26950} \tag{3.32}
\]

The essential of the previous conclusions is retrieved by the study.

### 3.2.1.2 Local Pressure-Dependent Cross-Flow

Berman and Green flows are now “extended” to the more representative problem of non-uniform pure-solvent leakage depending linearly on the local pressure as shown in Figure 3.5.

Since the pressure on the downstream side of the membrane is set to zero, the local permeate flux, \(U(z)\), depends on the local feed-side pressure only, \(P(z)\). As in Darcy-Starling’s law\(^{15}\), this dependence is assumed to be linear [Haldenwang, 2007]. The proportionality is given by the membrane solvent permeability, \(I_0^{-1}\)

---

\(^{15}\) Or in the solution-diffusion model.
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(a) Cross-flow of pure solvent in a symmetric plane channel with axially varying, pressure-dependent permeation at the permeable walls. The channel half-height is \(d\) and the origin of the coordinate system is situated in the middle of the channel.

(b) Cross-flow of pure solvent in an asymmetric plane channel with axially varying, pressure-dependent permeation at the permeable wall. The channel full-height is \(d\) and the origin of the coordinate system is situated on the impermeable wall.

Figure 3.5: Cross-flow of pure solvent where permeation is dependent on the local pressure value. Drawing not to scale \((d \ll L)\).

\[ U(z) = \frac{P(z)}{I_0} = I_0^{-1} P(z) \]  

(3.33)

The dimensional analysis proposed by Haldenwang [2007] allows to describe the problem by means of four independent dimensionless numbers presented in Table 3.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Denomination</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Re_{in}^i)</td>
<td>inlet transverse Reynolds number</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>dimensionless pressure drop</td>
</tr>
<tr>
<td>(\tau)</td>
<td>reduced channel length</td>
</tr>
<tr>
<td>(\beta)</td>
<td>reduced membrane solvent permeability</td>
</tr>
</tbody>
</table>

Table 3.2: Four independent dimensionless numbers describe the pressure-dependent permeation of pure solvent.

Let \(U_{in}\) be the velocity of permeation of pure solvent at (only) the channel entrance.
From now on:

$$L_{de} = \frac{W_{in}d}{U_{in}}$$  \hspace{1cm} (3.34)

The number $\alpha$ compares the pressure drop to the feed pressure. Back to Table 3.2:

$$Re_{in}^l = \frac{\rho_0 U_{in}d}{\mu_0}$$  \hspace{1cm} (3.35)

$$U_{in} = I_0^{-1} P_{in}$$  \hspace{1cm} (3.36)

$$\tau \equiv \frac{L}{L_{de}}$$  \hspace{1cm} (3.37)

$$\alpha \equiv \left(\frac{\mu_0 W_{in}^2}{I_0^{-1} P_{in}^2 d}\right)^{1/2}$$  \hspace{1cm} (3.38)

$$\beta \equiv \frac{\mu_0 I_0^{-1}}{d}$$  \hspace{1cm} (3.39)

The problem’s variables and unknowns are they too expressed in non-dimensional form. Their order of magnitude is typically one at most.

$$x = \frac{X}{d} \quad z = \frac{Z}{L_{de}} \quad u = \frac{U}{U_{in}} \quad w = \frac{W}{W_{in}} \quad p = \frac{P}{P_{in}}$$  \hspace{1cm} (3.40)

Note in Equation 3.40 that $u$ is now reduced by $U_{in}$ (and not by $U_W$). The inlet transverse Reynolds number is related to the inlet longitudinal (or axial) Reynolds number, $Re_{in}^l$ by [Haldenwang, 2007]:

$$Re_{in}^l = Re_{in}^t \frac{\alpha}{\sqrt{\beta}}.$$  \hspace{1cm} (3.41)

In this new notation, the dimensionless Navier-Stokes equations in the domain $\omega = \{0 < x < 1\} \times \{0 < z < \tau\}$ are:

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$$  \hspace{1cm} (3.42)

$$Re_{in}^l \left( \frac{\partial u}{\partial x} + w \frac{\partial u}{\partial z} \right) = -\frac{1}{\beta} \frac{\partial p}{\partial x} + \frac{\partial^2 u}{\partial x^2} + \frac{\beta}{\alpha^2} \frac{\partial^2 u}{\partial z^2}$$  \hspace{1cm} (3.43)

$$Re_{in}^l \left( u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} \right) = -\frac{1}{\alpha^2} \frac{\partial p}{\partial z} + \frac{\partial^2 w}{\partial x^2} + \frac{\beta}{\alpha^2} \frac{\partial^2 w}{\partial z^2}$$  \hspace{1cm} (3.44)
The dimensionless velocities \( u \) and \( w \) have the same order of magnitude. From the equations above, the magnitude of the pressure gradients could hence be related by \( \| \partial p/\partial x \| \approx [\beta/\alpha^2]\| \partial p/\partial z \| \). In the case of walls of low permeability (membrane processes for instance), \( \beta \ll 1 \). In standard filtration moreover, the permeate flow is much lower than the axial flow, i.e. (from Equation 3.41) \( Re_{in}/Re_{in} \rightarrow 0 \) (or \( [U_{in}/W_{in}]^2 \ll 1 \)). In this limit, \( \partial p/\partial x \approx 0 \) and the pressure will vary along the axial coordinate \( z \) only, according to Equation 3.44. The same considerations show that \( [\beta/\alpha^2]\| \partial^2 w/\partial z^2 \| \ll \| \partial^2 w/\partial x^2 \| \), that is, the term of axial diffusion of momentum is negligible compared to the one of transverse diffusion. Under these considerations [Haldenwang, 2007], the system of equations above, equivalent to Prandtl’s boundary-layer equations [Schlichting, 1968], becomes.

\[
\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0 \tag{3.45}
\]
\[
Re_{in} \left( u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} \right) = -\frac{1}{\alpha^2} \frac{\partial p}{\partial z} + \frac{\partial^2 w}{\partial x^2} \tag{3.46}
\]

In “exchange” for minor losses in the problem’s description, these two hypotheses considerably simplify the momentum balance, rendering therefore an analytic solution for the system of equations more viable.

The resolution in a channel limited by two identical permeable walls (Figure 3.5a) was carried out by Haldenwang [2007]. The corresponding development for the channel limited by one permeable wall (Figure 3.5b) was undertaken in Bernales [2013].

Like before, the symmetric problem is solved in half of the channel, from the midplane to the wall. The boundary conditions in this case are:

\[
u(1, z) = p(1, z) = p(z) \quad u(0, z) = 0 \quad w(1, z) = 0 \quad \frac{\partial w}{\partial x}(0, z) = 0 \tag{3.47}
\]

As explained right after Equation 3.13, only the last of these conditions is modified in the asymmetric channel:

\[
u(1, z) = p(1, z) = p(z) \quad u(0, z) = 0 \quad w(1, z) = 0 \quad w(0, z) = 0 \tag{3.48}
\]

In both cases, the first boundary condition is readily deduced by combining the definitions of \( u \) and \( p \) (Equation 3.40) and Equation 3.36. Let \( q(z) \) be the normal-
ized flowrate (or dimensionless mean axial velocity):
\[ q(z) = \int_0^1 w(x, z) \, dx \] (3.49)

The negative of its derivative is actually equal to the local pressure:
\[ -q'(z) \equiv -\int_0^1 \frac{\partial w}{\partial z}(x, z) \, dx = \int_0^1 \frac{\partial u}{\partial x}(x, z) \, dx = u(1, z) = p(z) \] (3.50)

The extension of Berman’s and of Green’s solutions to the case of non-uniform permeation leads each to an ordinary differential equation of the variables \( q \), \( q' \) and \( q'' \) in the form of infinite perturbation series of \( Re_{in}^t \). The truncation of these expansions at rising orders results in approximate analytical solutions to the Navier-Stokes equations. The solutions are ordinary differential equations of growing complexity and, in principle, accuracy, describing the flowrate in the channels. At zeroth\(^{16}\), first and second orders respectively, they are:

\[ q'' - 3\alpha^2 q = 0 \] (3.51)
\[ q'' - \alpha^2 q(k_0 - k_1 Re_{in}^t q') = 0 \] (3.52)
\[ q'' - k_0 \alpha^2 q \left( 1 - \frac{k_1}{k_0} Re_{in}^t q' + \frac{k_2}{2k_0} (Re_{in}^t)^2 q'^2 \right) = 0 \] (3.53)

The constants \( k_0 \), \( k_1 \) and \( k_2 \) are equal, respectively, to 3, -81/35 and 468/13475 for Berman’s geometry and to 12, -81/35 and 2929/26950 for Green’s configuration.

It is worth clarifying that the Berman and Green flows are themselves solutions of their respective “extended” models for the specific case where the flows are isobaric along the entire walls. This happens for \( Re_{in}^t = 1.3107 \) [Haldenwang, 2007] in the symmetric channel and \( Re_{in}^t = 6.30388 \) [Bernales, 2013] in the asymmetric geometry.

In addition to their evident quantitative interest when dealing with problems of liquid permeation, Equation 3.52 and Equation 3.53 provide quantitative bases for the study of important phenomena (“hydrodynamic accidents”) that might occur in long enough (> \( \tau \)) symmetric and asymmetric channels with permeable walls:

• Axial flow exhaustion (AFE) when the axial flow is extincted due to excessive permeatio before the channel’s end is reached [Bernales, 2013; Haldenwang, 2007];

• Cross-flow reversal (CFR) when the viscous drop reduces the inner pressure below the external pressure, stopping suction and allowing injection of filtrate into the channel [Bernales, 2013; Haldenwang, 2007];

• Pressure runaway downstream the flow channel (\(\partial p/\partial z > 0\)) when “the flow decelerates faster than it rubs”, i.e., a situation where the viscous pressure drop is exceeded along the channel by the inertial pressure enhancement consequent to the axial deceleration of the fluid (deceleration precipitated by permeation) [Haldenwang and Guichardon, 2011].

The analogous study in cylindrical coordinates for an axisymmetric leaky pipe\(^{17}\) (a hollow fiber membrane, for example) is performed in Bernales [2013] and Bernales and Haldenwang [2014]

### 3.2.2 Analytical Modeling of Hydrodynamics and Bulk Mass Transfer

A further step in modeling membrane filtration is made when a *solution* is considered because the mass transfer of solute needs to be coupled to the pure hydrodynamic problem, giving rise, in other words, to the description of concentration polarization. In the following, the walls are impermeable to the solute\(^{18}\) (unitary rejection rate). We analyze the problems in the framework of Berman and Green flows. Sketches of both cases are presented in Figure 3.6.

The essential of the findings and notation of the previous sections is kept. Two dimensional parameters are still needed: the molar concentration and the diffusion coefficient of the solute in the feed, \(C_{in}\) and \(D_0\). Additional parameters may be necessary on a case-by-case basis for calculating the osmotic pressure.

The Navier-Stokes equations (Equations 3.12 and 3.13) for a steady system with constant properties are complemented by the conservation (continuity) equation for the solute\(^{19}\), which describes the solute transport by diffusion and by convection

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\(^{17}\) Based on Yuan and Finkelstein flow: S. W. Yuan and A. B. Finkelstein in “Laminar pipe flow with injection and suction through a porous wall” (Trans. ASME, 78 (1956) pp. 719-724).

\(^{18}\) This hypothesis will be relaxed later on.

\(^{19}\) Without chemical reaction.
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(a) Mass transfer coupled to Berman flow leading to concentration polarization. \( d \) is the channel half-height and the origin of the coordinate system is situated in the middle of the channel.

(b) Mass transfer coupled to Green flow leading to concentration polarization. \( d \) is the channel full-height and the origin of the coordinate system is situated on the impermeable wall.

Figure 3.6: Berman and Green flows coupled to solute bulk solute mass transfer. Drawing not to scale (\( d \ll L \)).

in all directions simultaneously. Noting \( C(X, Z) \) its scalar concentration field:

\[
(V \cdot \nabla)C = D_0 \Delta C
\]  
(3.54)

Some parameters need to be defined for the coming analyses. The osmotic pressure of the feed stream, \( \Pi_{in}^{osm} \), follows van’t Hoff’s law and leads to the definition of an osmotic counter-permeate flux \( U_{in}^{osm} \):

\[
\Pi_{in}^{osm} = iRTC_{in} = \Gamma C_{in}
\]  
(3.55)

\[
U_{in}^{osm} = I_{in}^{-1}\Pi_{in}^{osm} = I_{in}^{-1}\Gamma C_{in}
\]  
(3.56)

The van’t Hoff factor is \( i \), \( T \) is the temperature of the solution, \( R \) the universal gas constant and \( \Gamma \) the osmotic factor.

Now, \( \rho_0 \) and \( \mu_0 \) designate the density and the dynamic viscosity of the feed solution instead of those of the pure solvent. New dimensionless parameters [Haldenwang et al., 2010] are introduced: firstly, the (transverse) Reynolds number of uniform permeation subject to concentration polarization and osmosis, and the Schmidt
number $Sc$:

\[
Re^t_0 \equiv \frac{\rho_0 U_0 d}{\mu_0}
\]

\[
Sc \equiv \frac{\mu_0}{\rho_0 D_0}
\]  

(3.57)  

(3.58)

$U_0$ is the unknown, uniform permeate flux under concentration polarization and osmosis in Figure 3.6.

Some parameters will be expressed differently. The so-called inlet pure solvent transverse Péclet number, $Pe_{in}$, is a dimensionless form of the applied pressure. The inlet osmotic Péclet number becomes the dimensionless feed concentration. The permeation Péclet number, $Pe_0$, is the dimensionless permeate flux (unknown). Summing up, the “3 Péclet numbers” are [Haldenwang et al., 2010]:

\[
Pe_{in} \equiv Re^t_{in} \quad Sc = \frac{U_{in} d}{D_0} = P_{in} \left( \frac{I_0^{-1} d}{D_0} \right)
\]

(3.59)

\[
Pe_{in}^{osm} \equiv \frac{U_{in}^{osm} d}{D_0} = C_{in} \left( \frac{\Gamma I_0^{-1} d}{D_0} \right)
\]

(3.60)

\[
Pe_0 \equiv Re^t_0 \quad Sc = U_0 \left( \frac{d}{D_0} \right)
\]

(3.61)

$Pe_{in}$ is an upper bound of any Péclet number and gives the scale of reference for the other permeation velocities.

And to conclude the listing\(^{20}\):

\[
x = \frac{X}{d} \quad z = \frac{Z}{L_{de}} \quad u = \frac{U}{U_0} \quad w = \frac{W}{W_{in}} \quad c = \frac{C}{C_{in}}
\]

(3.62)

As mentioned, the case of uniform permeation throughout the length of the channel’s walls is analyzed. This requires that the pressure remain essentially constant along the flow channel – in other words, that the pressure drop be negligible compared to the operating pressure, i.e., $\alpha \ll 1$. This “high pressure” condition (HP) is satisfied in typical RO and NF. In these processes, pressure drops of about $10^4$ Pa contrast with operating pressures of several MPa.

Table 3.3 summarizes the independent dimensionless numbers of the new problem:

---

\(^{20}\) Note the denominator $U_0$ in the third expression, and not $U_{in}$ as in Equation 3.40. Actually, because the permeate flux is constant now, the former $U_0$ is equivalent to the current $U_{in}$.  

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Parameter | Denomination
--- | ---
$Re_0^t$ | transverse Reynolds number for homogeneous permeation
$Sc$ | Schmidt number
$Pe_{in}$ | inlet pure solvent transverse Péclet number (dimensionless applied pressure)
$Pe_{osm}{in}$ | inlet osmotic Péclet number (dimensionless feed concentration)
$Pe_0$ | permeation Péclet number (dimensionless permeate flux)

Table 3.3: Four independent dimensionless numbers describe the coupled hydrodynamic-bulk mass transfer problem with uniform permeation and totally solute-rejecting walls: $Re_0^t$, $Sc$, $Pe_{in}$ and $Pe_{osm}{in}$. The two first can be merged into a single parameter: $Pe_0$.

Under the HP hypothesis and considering the mass diffusion in the axial direction to be negligible [Haldenwang et al., 2010; Kim, 2007; Zeman and Zydny, 1996, p. 353] (a “Prandtl version” [Haldenwang et al., 2010] of the solute conservation law 3.63), an exact solution to the problem of solute advection by Berman flow subject to osmotic effects was developed by Haldenwang et al. [2010].

The solute mass balance (Equation 3.54) combined with Berman flow reads in dimensionless form:

$$Pe_0 \left[ B(x, Re_0^t) \frac{\partial c}{\partial x} + (1 - z)B'(x, Re_0^t) \frac{\partial c}{\partial z} \right] = \frac{\partial^2 c}{\partial x^2} \tag{3.63}$$

For a totally solute-rejecting membrane, the mass balance on the membrane surface equals the solute carried downward by convection to that diffusing back into the bulk. Considering, as already mentioned, an axially symmetric concentration profile, the boundary conditions are:

$$\frac{\partial c}{\partial x}(1, z) = c(1, z)Pe_0 \quad \frac{\partial c}{\partial x}(0, z) = 0 \tag{3.64}$$

The exact solution for the solute concentration profile under these conditions is:

$$c(x, z) = \frac{1}{1 - z} \exp \left[ Pe_0 \int_0^x B(\hat{x}, Re_0^t) d\hat{x} \right] \tag{3.65}$$

$$\int_0^x B(\hat{x}, Re_0^t) d\hat{x} = \sum_{n=0}^{\infty} \frac{1}{n!} F_n(x)(Re_0^t)^n \tag{3.66}$$

Where $F_n(x)$ are the primitives of the coefficients deducted from the expansion of
Berman’s solution in series (Equations 3.22 and 3.23), with:

\[
F_0(x) = \frac{3x^2}{4} - \frac{x^4}{8} \quad F_1(x) = \frac{1}{280} \left( -x^2 + \frac{3x^4}{4} - \frac{x^8}{8} \right)
\]  

(3.67)

For \( n = 0 \), the transverse concentration profile normalized by the local wall surface concentration, \( c_W(z) \), is independent of \( z \):

\[
c(x,z) = c_W(z) = \exp \left[ \frac{P_e_0}{8} (-x^4 + 6x^2 - 5) \right]
\]  

(3.68)

By plotting \( c(x,z)/c_w(z) \) across the channel height for different permeation Péclet numbers, the authors showed that the physical postulate of the film theory (section 3.1.2.2), namely a thin boundary layer compared to the channel height, holds for higher permeations only, \( P_e_0 \geq \Theta(10) \). For lower values, a marked concentration profile exists all across the channel.

If, hypothetically, the transverse concentration profile is imposed constant along the flow channel, it is being implied that the permeate volumetric recovery compared to the total feed cannot be excessive, otherwise the axial uniformity of the bulk concentration would not be possible. This was termed “low recovery” (LR) condition. It ensures that the osmotic counter-pressure across the membrane will not vary axially either. Noting that \( U_0L \) is the total volumetric flow rate of permeate and that \( W_{in}d \) is the total feed flow rate, LR requires \( \tau = (U_0L)/(W_{in}d) \ll 1 \) [Haldenwang et al., 2010].

The wall surface concentration under conditions of axially uniform concentration polarization and osmotic effects was approximated from the previous equations at zeroth order on \( Re_0 \) by considering \( (1 - z) \ll 1 \) (from \( \tau \ll 1 \) in HP-LR); it is noted \( c_W \). When rearranged for isolating the permeate flux, interestingly, its expression bears a resemblance with Equation 3.4 from the film theory:

\[
P_e_0 \approx \frac{8}{5} \ln c_W
\]  

(3.69)

Equation 3.69 is still used for linking the “3 Péclet numbers” to each other in a very concise way by assuming for the permeate flux a linear dependence on the difference between the operating pressure and the osmotic pressure\(^{21} \). In this case,

\(^{21}\) As suggested, for instance, by the solution-diffusion model and the osmotic pressure models.
algebraic rearrangements lead to:

$$\ln \left( \frac{Pe_{in} - Pe_0}{Pe_{in}^{osm}} \right) = \frac{5}{8} Pe_0$$

(3.70)

Equation 3.70 is easily visualized in the convenient “3 Péclet numbers diagram” of Figure 3.7.

The diagram shows that the permeate flow is zero as long as the operating pressure does not surpass the osmotic pressure on the feed side. For lower feed concentration, the plots are practically linear in a considerable range of pressure values. However, as concentration rises, the permeate flow is inflected at much lower pressures. This trend is due to the reduction of the effective pressure difference by the increasing osmotic counter-effect when concentration polarization becomes severer.

Focusing on processes for which $Pe_{in} \gg 1$ is a typical input value (higher than 10 for example) and the permeation is strongly hindered through the combined effects of osmosis and concentration polarization, \textit{i.e.} $Pe_{in} \gg Pe_0$, it was demonstrated [Haldenwang et al., 2010] for HP-LR conditions that polarization leads to a concentration on the membrane surface whose value only little deviates from the limit concentration which would exactly balance the operating pressure out. The short deviation between both concentration values can be calculated if the expansion of Equation 3.70 under the considerations above in a series of $Pe_{in}$ is pushed up to higher orders. The remarkable consequence is the appearance of the
limit flux phenomenon proportional to the transmembrane pressure and given in dimensional form by:

$$U_0 = \frac{8}{5} \frac{I_0^{-1} P_{in}}{P_{e_in}} \ln \left( \frac{P_{e_in}}{P_{e_osm}} \right)$$  \hspace{1cm} (3.71)$$

The analogous analytical study for the Green flow was carried out in Bernales [2013]. The non-dimensional solute conservation equation is in this case:

$$P e_0 \left[ G(x, Re_0) \frac{\partial c}{\partial x} + (1 - z)G'(x, Re_0) \frac{\partial c}{\partial z} \right] = \frac{\partial^2 c}{\partial x^2}$$  \hspace{1cm} (3.72)$$

The boundary condition for the solute concentration on the permeable wall is the same as in the previous paragraphs (first expression in Equation 3.64): mass balance for a perfectly rejecting membrane. Since the other wall is impermeable, the second boundary condition in Equation 3.64 imposed a flat concentration profile on it. More precisely:

$$\frac{\partial c}{\partial x} (1, z) = c(1, z) P e_0 \quad \frac{\partial c}{\partial x} (0, z) = 0$$  \hspace{1cm} (3.73)$$

The solute concentration profile is therefore described by:

$$c(x, z) = \frac{1}{1 - z} \exp \left[ P e_0 \int_0^x G(\hat{x}, Re_0) d\hat{x} \right]$$  \hspace{1cm} (3.74)$$

$$\int_0^x G(\hat{x}, Re_0) d\hat{x} = \sum_{n=0}^{\infty} \frac{1}{n!} F_n(x) (Re_0)^n$$  \hspace{1cm} (3.75)$$

The functions $F_n(x)$ are the antiderivatives of the coefficients deducted from Green’s solution expanded in series (Equations 3.30 and 3.31), with:

$$F_0(x) = x^3 - \frac{x^4}{2} \quad F_1(x) = -\frac{8}{105} x^3 + \frac{27}{280} x^4 - \frac{1}{20} x^6 + \frac{1}{35} x^7 - \frac{1}{140} x^8$$  \hspace{1cm} (3.76)$$

For $n = 0$:

$$\frac{c(x, z)}{c_W(z)} = \exp \left[ \frac{P e_0}{2} (-x^4 + 2x^3 - 1) \right]$$  \hspace{1cm} (3.77)$$

At lowest order and for $(1 - z) \ll 1$:

$$P e_0 \approx 2 \ln c_W$$  \hspace{1cm} (3.78)$$

The coefficient 2 indicates that the permeation velocity in Green flow is higher
than in Berman flow for same conditions of polarization, for which case the proportionality between $Pe_0$ and $\ln c_W$ is at $8/5$ (cf. Equation 3.69). In fact, these coefficients are equivalent to the mass transfer coefficient or Sherwood number of the film model (where they are unknown!) [Bernales, 2013]. The permeate flow remains nevertheless higher in the Berman problem because it has two permeable surfaces, one more than Green flow.

As for the “3 Péclet numbers”:

$$\ln \left( \frac{Pe_{\text{in}} - Pe_0}{Pe_{\text{osm}}^{\text{in}}} \right) = \frac{1}{2} Pe_0 \quad (3.79)$$

The film-type concentration profile for $Pe_0 \geq 0(10)$, the diagram of “3 Péclet numbers” and the limit flux phenomena (with a coefficient 2 instead of 8/5 in Equation 3.71) are also conclusions of the study.

An analogous study in cylindrical coordinates coupling hydrodynamics and solute mass transfer in a porous pipe was undertaken in Bernales [2013].

The progressive and unified approach adopted for solving hydrodynamic and mass transfer problems of increasing complexity proved to be very appropriate for providing, within its assumptions, solid theoretical and mathematical background for important characteristics applicable to membrane processes (and others): locally varying, pressure-dependent permeation; concentration polarization; influence of osmotic counter-effects; limit permeate flux; hydrodynamic accidents; differences between profiles in leaking and non-leaking ducts or symmetric and asymmetric channels; range of values for which the simplified film model is valid etc. It also shows that, to considerably far extent, it is not necessary to treat all these phenomena disconnectedly: up to this point, the mathematical description of the coupling of hydrodynamics and bulk mass transfer should suffice.

The Prandtl hypotheses and the dimensional analysis are convenient for the mathematical treatment and useful for analyzing the problem since many physical parameters need to be considered. For this reason they have been kept for treating the problems discussed in the coming pages.
3.2.3 Numerical Modeling of Hydrodynamics and Bulk Mass Transfer

Higher complexity and comprehensiveness are reached when the permeate flux, concentration polarization and osmotic effects all vary in the axial direction in a deeply coupled manner. At this level of refinement, the analytical resolution of the partial differential equations governing the problem is far from easy and a numerical approach is called for. At this point, the walls are still considered impermeable to the solute\textsuperscript{22}.

### 3.2.3.1 Problem Statement

Figure 3.8 illustrates the new problem. A solution is fed at the channel entrance and flows along the channel. Part of it permeates, the rest exiting the channel as retentate. Profiles originate naturally for all variables. For the time being, we analyze the symmetric geometry with two equally permeable walls.

![Figure 3.8](image)

Figure 3.8: Mass transfer coupled to local, pressure-dependent cross-flow with solute-impermeable walls (i.e., the permeate concentration is zero and rejection is total). In the symmetric configuration, \(d\) is the channel half-height and the origin of the coordinate system is situated in the middle of the channel. Drawing not to scale (\(d \ll L\)).

The osmotic number, or reduced feed concentration, \(N_{osm}\), has not yet been introduced. Its definition makes use of vant’ Hoff’s law (Equation 3.55):

\[
N_{osm} \equiv \Pi_{osm}^{in} = \frac{P_{e_{osm}}^{in}}{P_{e_{in}}} = \frac{iRTC_{in}}{P_{in}} \quad (3.80)
\]

Table 3.4 summarizes all the parameters of the new problem, highlighting thereby the reduction in the number of parameters achieved by the nondimensionalization.

\textsuperscript{22} This hypothesis will be relaxed in the next section.
CHAPTER 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

<table>
<thead>
<tr>
<th>Dimensional parameters</th>
<th>$P_{in}$</th>
<th>$C_{in}$</th>
<th>$W_{in}$</th>
<th>$d$</th>
<th>$L$</th>
<th>$I_0^{-1}$</th>
<th>$\rho_0$</th>
<th>$\mu_0$</th>
<th>$D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionless parameters</td>
<td>$Re_{in}$ (3.35)</td>
<td>$Pe_{in}$ (3.59)</td>
<td>$\alpha$ (3.38)</td>
<td>$N_{osm}$ (3.80)</td>
<td>$\tau$ (3.37)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4: Nine dimensional and five dimensionless parameters characterize the numerical model for cross-flow and bulk mass transfer under Prandtl hypotheses and with totally solute-rejecting walls.

The density, dynamic viscosity and solute diffusion coefficient in the feed, $\rho_0$, $\mu_0$ and $D_0$, are constant. This is a simplifying assumption. Given however the low magnitude of concentration polarization moduli in RO and NF in main applications (e.g. desalination), whose solutions show a weak dependence on the solute mass fraction, the assumption is coherent, all the more since higher polarization concerns a thin zone contiguous with the walls.

The dimensional variables and unknowns from the previous pages are considered: $X$, $Z$, $U$, $W$, $P$ and $C$. Their dimensionless forms are:

$$
\begin{align*}
x &= \frac{X}{d} \\
z &= \frac{Z}{L_{de}} \\
u &= \frac{U}{U_{in}} \\
w &= \frac{W}{W_{in}} \\
p &= \frac{P}{P_{in}} \\
c &= \frac{C}{C_{in}}
\end{align*}
$$

Like before, a Newtonian fluid with constant properties (a solution of one solvent and one solute) in fully-developed steady, incompressible, laminar flow in the domain $\omega = \{0 < x < 1\} \times \{0 < z < \tau\}$ is considered. Recapping the dimensionless Navier-Stokes equations and introducing the general continuity equation for the solute under Prandtl hypotheses:

$$
\begin{align*}
\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} &= 0 \\
\frac{\partial p}{\partial x} &= 0 \\
Re_{in} \left( u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} \right) &= -\frac{1}{\alpha^2} \frac{\partial p}{\partial z} + \frac{\partial^2 w}{\partial x^2} \\
Pe_{in} \left( u \frac{\partial c}{\partial x} + w \frac{\partial c}{\partial z} \right) &= \frac{\partial^2 c}{\partial x^2}
\end{align*}
$$
The boundary conditions in the domain $\omega$ are:

\[
\begin{align*}
  u(1, z) &= p(1, z) - N_{osm}c(1, z) & u(0, z) &= 0 \\
  w(1, z) &= 0 & \frac{\partial w}{\partial x}(0, z) &= 0 \\
  \frac{\partial c}{\partial x}(1, z) &= u(1, z)c(1, z)P_{c_{in}} & \frac{\partial c}{\partial x}(0, z) &= 0 \\
\end{align*}
\] (3.86)

### 3.2.3.2 Numerical Formulation

The numerical treatment hereafter has been developed by P. Haldenwang and first formalized in Bernales [2013]. In the following, it will be explained in detail. An overview of the calculation sequence is readily seen in Figure 3.10 which synthetizes the (also more compact) section 3.2.3.4.

Regular meshes of size $\Delta x$ and $\Delta z$ discretize, respectively, the transverse ($x$) and axial ($z$) computational domain $\omega = \{0 < x < 1\} \times \{0 < z < \tau\}$ from the grid point $j = 0$ up to $j = J$ and from $n = 0$ up to $n = N$:

\[
\begin{align*}
  x &= j\Delta x & \text{for} & & 0 \leq j \leq J & \text{where} & & \Delta x = 1/J \\
  z &= n\Delta z & \text{for} & & 0 \leq n \leq N & \text{where} & & \Delta z = \tau/N
\end{align*}
\] (3.87)

(3.88)

The profiles of all variables being known in the position $z = n\Delta z$, the numerical scheme is aimed at calculating their values in the next section, $z = (n + 1)\Delta z$. In order to do so, the derivatives in the longitudinal direction need to be approximated to some order $\xi$. For instance:

\[
\frac{\partial w_j^{(n+1)}}{\partial z} \approx \frac{1}{\Delta z} \sum_{\zeta=0}^{\xi} \sigma_{\zeta}w_j^{(n+1-\zeta)}
\] (3.89)

The coefficients $\sigma_{\zeta}$ vary according to the discretization scheme adopted and will be defined further on.

In semi-discrete form, the Navier-Stokes equation (Equation 3.84) and the solute...
conservation equation (Equation 3.85) read:

\[
Re_{in} \hat{w}_j^{(n+1)} \frac{\sigma_0}{\Delta z} w_j^{(n+1)} - \frac{\partial^2 w_j^{(n+1)}}{\partial x^2} + \frac{1}{\alpha^2} \frac{\sigma_0}{\Delta z} p_j^{(n+1)} =
\]

\[
- Re_{in} \hat{w}_j^{(n+1)} \sum_{\zeta=1}^{\epsilon} \frac{\sigma}{\Delta z} w_j^{(n+1-\zeta)} - Re_{in} \hat{u}_j^{(n+1)} \frac{s_{w_j}^{(n+1)}}{\partial x} - \frac{1}{\alpha^2} \sum_{\zeta=1}^{\epsilon} \frac{\sigma}{\Delta z} p_j^{(n+1-\zeta)} \tag{3.90}
\]

\[
P_{e_{in}} \hat{w}_j^{(n+1)} \frac{\sigma_0}{\Delta z} c_j^{(n+1)} - \frac{\partial^2 c_j^{(n+1)}}{\partial x^2} =
\]

\[
- P_{e_{in}} \hat{w}_j^{(n+1)} \sum_{\zeta=1}^{\epsilon} \frac{\sigma}{\Delta z} c_j^{(n+1-\zeta)} - P_{e_{in}} \hat{u}_j^{(n+1)} \frac{s_{c_j}^{(n+1)}}{\partial x} \tag{3.91}
\]

Symbol ^ designates quantities inferred by linear extrapolation \[\frac{\theta^{(n+1)} + \theta^{(n-1)}}{2} = \theta^{(n)}\]:

\[
\hat{w}_j^{(n+1)} \approx 2w_j^{(n)} - w_j^{(n-1)} \tag{3.92}
\]

\[
\hat{u}_j^{(n+1)} \approx 2u_j^{(n)} - u_j^{(n-1)} \tag{3.93}
\]

\[
\hat{c}_j^{(n+1)} \approx 2c_j^{(n)} - c_j^{(n-1)} \tag{3.94}
\]

Transverse derivatives are discretized by second-order centered finite-divided-difference schemes [Richtmyer and Morton, 1967, pp. 17, 190]:

\[
\frac{\partial w_j^{(n+1)}}{\partial x} \approx \frac{w_{j+1}^{(n+1)} - w_{j-1}^{(n+1)}}{2\Delta x} \tag{3.95}
\]

\[
\frac{\partial c_j^{(n+1)}}{\partial x} \approx \frac{c_{j+1}^{(n+1)} - c_{j-1}^{(n+1)}}{2\Delta x} \tag{3.96}
\]

\[
\frac{\partial^2 w_j^{(n+1)}}{\partial x^2} \approx \frac{w_{j+1}^{(n+1)} - 2w_j^{(n+1)} + w_{j-1}^{(n+1)}}{(\Delta x)^2} \tag{3.97}
\]

\[
\frac{\partial^2 c_j^{(n+1)}}{\partial x^2} \approx \frac{c_{j+1}^{(n+1)} - 2c_j^{(n+1)} + c_{j-1}^{(n+1)}}{(\Delta x)^2} \tag{3.98}
\]

Axial derivatives by second-order backward finite differences [Richtmyer and Morton, 1967, p. 190]:

\[
\frac{\partial w_j^{(n+1)}}{\partial z} \approx \frac{3w_{j+1}^{(n+1)} - 4w_j^{(n)} + w_{j-1}^{(n-1)}}{2\Delta z} \tag{3.99}
\]

\[
\frac{\partial c_j^{(n+1)}}{\partial z} \approx \frac{3c_{j+1}^{(n+1)} - 4c_j^{(n)} + c_{j-1}^{(n-1)}}{2\Delta z} \tag{3.100}
\]
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From which, by the way, we identify the coefficients $\sigma$ of Equation 3.89:

$$\sigma_0 = \frac{3}{2} \quad \sigma_1 = -2 \quad \sigma_2 = \frac{1}{2}$$

And the transverse velocity field is given by integrating the continuity equation:

$$0 = \int_{x}^{x+\Delta x} \left( \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) dx = u|_{x}^{x+\Delta x} + \int_{x}^{x+\Delta x} \frac{\partial w}{\partial z} dx$$  \hspace{1cm} (3.101)

Approximated by the trapezoid rule:

$$u_{j+1}^{(n+1)} \approx u_j^{(n+1)} - \frac{\Delta x}{2} \left( \frac{\partial w}{\partial z} \bigg|_{j+1}^{(n+1)} + \frac{\partial w}{\partial z} \bigg|_{j}^{(n+1)} \right)$$  \hspace{1cm} (3.102)

Note from definition 3.87 that $x = 0$ is referred to with subscript 0 and $x = 1$ with subscript $J$. The discrete boundary conditions from Equation 3.86 read:

$$w_j^{(n+1)} = 0$$  \hspace{1cm} (3.103)

$$\left. \frac{\partial w}{\partial x} \right|_0 = 0$$  \hspace{1cm} (3.104)

$$P_e \eta u_j^{(n+1)} c_j^{(n+1)} = \left. \frac{\partial c}{\partial x} \right|_j^{(n+1)}$$  \hspace{1cm} (3.105)

$$\left. \frac{\partial c}{\partial x} \right|_0 = 0$$  \hspace{1cm} (3.106)

$$u_j^{(n+1)} = 0$$  \hspace{1cm} (3.107)

$$p_j^{(n+1)} - N_{osm} c_j^{(n+1)} + \frac{\sigma_0}{\Delta z} \sum_{j=0}^{J} \chi_j w_j^{(n+1)} = - \sum_{\zeta=1}^{\xi} \frac{\sigma_\zeta}{\Delta z} \left( \sum_{j=0}^{J} \chi_j w_j^{(n+1-\zeta)} \right)$$  \hspace{1cm} (3.108)

$\chi_0 = \chi_J = \Delta x/2$ and, for $1 \leq j \leq (J - 1)$, $\chi_j = \Delta x$. These coefficients come from the numerical implementation of the trapezoidal rule for the integration of the continuity equation across an entire cross-section followed by utilization of the conditions $u(1, z) = p(1, z) - N_{osm} c(1, z)$ and $u(0, z) = 0$ (from Equation 3.86). The boundary condition 3.108 is indeed necessary because of the additional unknown$^{23}$ $p^{(n-1)}$ in Equation 3.90.

$^{23}$ For this reason, incidentally, the hydrodynamic part of the problem still has a total of $J + 1$ unknowns even if the no-slip condition (Equation 3.103) implies that all values of axial velocity are already known at $j = J$ (they are zero).
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3.2.3.3 Discretization and Transverse Resolution

Complete discretization of Equation 3.91 and of Equation 3.90 within a same cross-section \( n + 1 \) results in two linear equations for each transverse grid point \( j \), sc. one for the concentration and one for the axial velocity\(^{24} \). We now show how the resolution of these systems of equations is carried out.

The profiles can be contracted into:

\[
A_1(j) c_{j-1}^{(n+1)} + B_1(j) c_j^{(n+1)} + C_1(j) c_{j+1}^{(n+1)} = R_1(j) \tag{3.109}
\]

\[
A_2(j) w_{j-1}^{(n+1)} + B_2(j) w_j^{(n+1)} + C_2(j) w_{j+1}^{(n+1)} + E(j) p^{(n+1)} = R_2(j) \tag{3.110}
\]

With, for \( 1 \leq j \leq J - 1 \):

\[
A_1(j) = -\frac{1}{(\Delta x)^2} \tag{3.111}
\]

\[
B_1(j) = Pe_{in} \frac{3}{2\Delta z} + \frac{2}{(\Delta x)^2} \tag{3.112}
\]

\[
C_1(j) = -\frac{1}{(\Delta x)^2} \tag{3.113}
\]

\[
R_1(j) = Pe_{in} \left[ \frac{\hat{w}_j^{(n+1)}}{\Delta z} \left( 2c_j^{(n)} - \frac{c_j^{(n-1)}}{2} \right) - \hat{u}_j^{(n+1)} \left( \frac{c_{j+1}^{(n+1)} - c_{j-1}^{(n+1)}}{2\Delta x} \right) \right] \tag{3.114}
\]

\[
A_2(j) = -\frac{1}{(\Delta x)^2} \tag{3.115}
\]

\[
B_2(j) = \frac{3}{2\Delta z} Re_t \frac{\hat{w}_j^{(n+1)}}{\Delta z} + \frac{2}{(\Delta x)^2} \tag{3.116}
\]

\[
C_2(j) = -\frac{1}{(\Delta x)^2} \tag{3.117}
\]

\[
E(j) = \frac{3}{2\alpha^2 \Delta z} \tag{3.118}
\]

\[
R_2(j) = Re_t \left[ \frac{\hat{w}_j^{(n+1)}}{\Delta z} \left( 2w_j^{(n)} - \frac{w_j^{(n-1)}}{2} \right) - \hat{u}_j^{(n+1)} \left( \frac{w_{j+1}^{(n+1)} - w_{j-1}^{(n+1)}}{2\Delta x} \right) \right] + \frac{1}{\alpha^2 \Delta z} \left( 2p^{(n)} - \frac{1}{2} p^{(n-1)} \right) \tag{3.119}
\]

Analogous terms must be written at \( j = 0 \) and \( j = J \) too. Discretization of the boundary condition 3.106 followed by its adaptation to the form of Equation 3.109

\(^{24}\) Where the pressure term \( p^{(n+1)} \) is included.
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gives:

\[ c_{-1}^{(n+1)} = c_1^{(n+1)} \] (3.120)
\[ C1(0) = -\frac{2}{(\Delta x)^2} \] (3.121)

Discretization of the boundary condition 3.105 followed by its adaptation to the form of Equation 3.109 gives:

\[ c_{J+1}^{(n+1)} = c_{J-1}^{(n+1)} + 2\Delta x P e_{in} \tilde{u}_{J}^{(n+1)} c_J^{(n+1)} \] (3.122)
\[ A1(J) = -\frac{2}{(\Delta x)^2} \] (3.123)
\[ B1(J) = Pe_{in} \left[ \frac{3}{2\Delta z} \tilde{w}_{J}^{(n+1)} - \frac{2}{\Delta x} \tilde{u}_{J}^{(n+1)} \right] + \frac{2}{(\Delta x)^2} \] (3.124)
\[ R1(J) = Pe_{in} \left[ \frac{\tilde{w}_{J}^{(n+1)}}{\Delta z} \left( 2c_{J}^{(n)} - \frac{c_{J}^{(n-1)}}{2} \right) - \left( \tilde{u}_{J}^{(n+1)} \right)^2 Pe_{in} \tilde{c}_J^{(n+1)} \right] \] (3.125)

Discretization of the boundary condition 3.104 followed by its adaptation to the form of Equation 3.110 gives:

\[ w_{-1}^{(n+1)} = w_1^{(n+1)} \] (3.126)
\[ C2(0) = -\frac{2}{(\Delta x)^2} \] (3.127)

The discretization of the boundary condition 3.108 gives:

\[ \left( \frac{3\Delta x}{4\Delta z} \right) w_0^{(n+1)} + \left( \frac{3\Delta x}{2\Delta z} \right) \sum_{j=1}^{J-1} w_j^{(n+1)} + p^{(n+1)} = \]
\[ N_{osm} \tilde{c}_J^{(n+1)} + \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right) \sum_{j=1}^{J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_{j}^{(n)} - \frac{1}{2} w_{j}^{(n-1)} \right) \right] \] (3.128)

This expression can be rewritten as (it will be soon shown why):

\[ D2(0)w_0^{(n+1)} + \sum_{j=1}^{J-1} D2(j)w_j^{(n+1)} + D2(J)p^{(n+1)} = R2(J) \] (3.129)
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Where:

\[ D_2(0) = \frac{3\Delta x}{4\Delta z} \]  
(3.130)

\[ D_2(j) = \frac{3\Delta x}{2\Delta z} \quad \text{for} \quad 1 \leq j \leq J - 1 \]  
(3.131)

\[ D_2(J) = 1 \]  
(3.132)

\[ R_2(J) = N_{osm}c_J^{(n+1)} + \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2}w_0^{(n-1)} \right) \]
\[ + \sum_{j=1}^{J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2}w_j^{(n-1)} \right) \right] \]  
(3.133)

Note furthermore that \( A_1(0) = A_2(0) = 0 \) and that \( B_1(0), R_1(0), B_2(0), E(0) \) and \( R_2(0) \) have the same form as in Equations 3.112, 3.114, 3.116, 3.118 and 3.119. These definitions having been presented, the systems of linear equations 3.109 and 3.110 can be solved.

The coefficient matrix of Equation 3.109 is tridiagonal of dimension \((J+1) \times (J+1)\) composed of \( A_1, B_1 \) and \( C_1 \); \( R_1 \) contains only constant terms and \( c_j^{(n+1)} \) is the vector of unknowns.

\[
\begin{bmatrix}
B_1(0) & C_1(0) & 0 & 0 & \cdots & 0 \\
A_1(1) & B_1(1) & C_1(1) & 0 & \cdots & 0 \\
0 & A_1(2) & B_1(2) & C_1(2) & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & A_1(J) & B_1(J)
\end{bmatrix}
\begin{bmatrix}
c_0^{(n+1)} \\
c_1^{(n+1)} \\
c_2^{(n+1)} \\
\vdots \\
c_J^{(n+1)}
\end{bmatrix}
= 
\begin{bmatrix}
R_1(0) \\
R_1(1) \\
R_1(2) \\
\vdots \\
R_1(J)
\end{bmatrix}
\]  
(3.134)

The system 3.134 is solved using Lower-Upper decomposition. The result is a concentration value at each grid point of the cross-section in question.

The coefficient matrix of Equation 3.110 is composed of a tridiagonal submatrix of dimension \((J+1) \times (J+1)\) containing \( A_2, B_2 \) and \( C_2 \) and, additionally, of a last column filled with the coefficients \( E \) and of a last row of coefficients \( D_2 \). The vector of unknowns includes the velocity field \( w_j^{(n+1)} \) for \( 0 \leq j \leq J - 1 \) and the
The system 3.135 is solved using Gaussian elimination followed by Lower-Upper factorization. The results are the axial velocity field $w_{j}^{(n+1)}$ and the pressure value $p_{j}^{(n+1)}$ in the cross-section in question.

The calculation of the transverse velocity field, $u_{j}^{(n+1)}$, is now possible by combining the continuity equation 3.102 and Equation 3.99.

### 3.2.3.4 Iterative Implementation and Convergence

The mathematical resolution having been described, we explain the sequence of calculations. Before, a commentary deserves to be done.

The inherent nonlinearity of the transport equations is increased by the Robin boundary condition (Equation 3.105). It couples permeation velocity and concentration nonlinearly “in return” for the determination of the concentration polarization phenomenon. On top of it, another boundary condition is imposed to $u$, this time the condition of permeation (Equation 3.108). Therefore, $u$ deserved a particular attention inasmuch as it is, actually, calculated iteratively. Let $U^{(k)}$ be a series ($k = 0, 1, 2, 3...$) of estimates of the sought-for permeation velocity $u_{j}^{(n+1)}$. When convergence is reached, $\lim U^{(k)} = u_{j}^{(n+1)}$ (see criterion 3.137).

The algorithm implemented for this purpose is schematized in Figure 3.10. The sequence of calculations starts in the cross-section $n = 0$ by assigning profiles to the entry flow: $u_{j}^{(0)}$, $w_{j}^{(0)}$, $c_{j}^{(0)}$ and $p^{(0)}$. The second-order partial differential equations being parabolic under Prandtl conditions, initial conditions need to be assigned to the channel’s entrance. Typically, transversally unitary pressure and concentration profiles are used together with Berman (Equation 3.26) or Hagen-Poiseuille velocity profiles, but other profiles are acceptable. For $n = 1$, where the profiles are still not known definitely, estimations are done with extrapolated

\[ \begin{bmatrix} B2(0) & C2(0) & 0 & 0 & \cdots & E(0) \\ A2(1) & B2(1) & C2(1) & 0 & \cdots & E(1) \\ 0 & A2(2) & B2(2) & C2(2) & \cdots & E(2) \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ D2(0) & D2(1) & D2(2) & D2(3) & \cdots & D2(J) \end{bmatrix} \times \begin{bmatrix} w_0^{(n+1)} \\ w_1^{(n+1)} \\ w_2^{(n+1)} \\ \vdots \\ \vdots \\ p^{(n+1)} \end{bmatrix} = \begin{bmatrix} R2(0) \\ R2(1) \\ R2(2) \\ \vdots \\ \vdots \\ R2(J) \end{bmatrix} \]
values: $\hat{u}_j^{(n+1)}$, $\hat{w}_j^{(n+1)}$, $\hat{c}_j^{(n+1)}$ and $\hat{p}^{(n+1)}$. This presupposes the previous knowledge of hypothetic values at $n = -1$, $u_j^{(-1)}$, $w_j^{(-1)}$, $c_j^{(-1)}$ and $p^{(-1)}$, which are set equal to those at $n = 0$. The first iteration in this section has been carried out: $U^{(k=0)} = \hat{u}_j^{(n+1)}$.

This done, the axial loop is launched. The following holds for all cross-sections $z = (n+1)\Delta z$ comprised between $n = 0$ an $n = N - 1$. Initially, the concentration field $c_j^{(n+1)}$ is solved (Equation 3.91). This stage is followed by the resolution of the hydrodynamic equations: first the calculation of the axial velocity and pressure profiles (Equation 3.90), $w_j^{(n+1)}$ and $p_j^{(n+1)}$, and then of the transverse velocity profile $u_j^{(n+1)}$ (Equation 3.102) as we have just seen.

At this point, it is possible to calculate the transverse velocity $U^{(k+1)}$ that must satisfy, at the membrane surface, the boundary condition relative to the permeation of solvent. The new value is obtained with the pressure and concentration values just calculated:

$$U^{(k+1)} = p^{(n+1)} - N_{osm}c_j^{(n+1)} \tag{3.136}$$

Now, the convergence criterion on the permeation velocity $u_j^{(n+1)}$ is checked. Designating $\varepsilon_{conv}$ a certain criterion of convergence (here set to $10^{-7}$), the test of convergence is:

$$\left| \frac{U^{(k)} - U^{(k+1)}}{U^{(k)}} \right| \leq \varepsilon_{conv} \tag{3.137}$$

If the condition is verified, the profiles just calculated for $n + 1$ are appropriate and can therefore be used for preparing the calculations on the next ("new") cross-section by updating the memories affected to $n - 1$, $n$ and $n + 1$. On the one hand, the values in the new section $n - 1$ will be updated with the profiles of the just calculated cross-section $n$. On the other hand, the profiles just calculated for section $n + 1$ will correspond to those of the new cross-section $n$. In other terms:

$$c_j^{(n-1)} \leftarrow c_j^{(n)} \quad w_j^{(n-1)} \leftarrow w_j^{(n)} \quad p^{(n-1)} \leftarrow p^{(n)} \quad u_j^{(n-1)} \leftarrow u_j^{(n)} \quad U^{(k)} \leftarrow U^{(k+1)} \tag{3.138}$$

If convergence is not attained, the iterative loop is launched until a value for $u_j^{(n+1)} = \lim U^{(k)}$ satisfies the criterion for convergence. For each new iteration, $k + 1$, the new guess of permeation velocity is done by updating the value of the variable according to $U^{(k)} = U^{(k)} + \omega(U^{(k)} - U^{(k+1)})$ where $\omega$ is a relaxation factor (here set to 0.15) introduced in order to accelerate convergence.
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The implementation has been done by means of an in-house Fortran programming code.

3.2.3.5 Asymmetric Flow Channel

The previous sections considered a symmetric flow channel with two equally permeable walls. If an asymmetric configuration with one permeable and one impermeable wall is considered, as for instance the one of Green flow, the numerical development, resolution and the algorithm remain the same, except for the following points:\(^{26}\):

- The calculation over the entire channel height according to the new definition of \(d\);
- The disappearance of the Neumann boundary condition at the middle of the center which implicated \(w^{(n+1)}_l = w^{(n+1)}_r\), now replaced by another no-slip condition, \(w_0 = 0\)^{27};
- This new boundary condition suppresses the first line of the matrix 3.135, because it is already known, but the resolution of the systems is not altered.

This problem is sketched in Figure 3.9.

Figure 3.9: Mass transfer coupled to local, pressure-dependent cross-flow with solute-impermeable walls (i.e., the permeate concentration is zero and rejection is total). In the asymmetric configuration, \(d\) is the channel full-height and the origin of the coordinate system is situated on the impermeable wall. Drawing not to scale (\(d \ll L\)).

---

\(^{26}\) A development in cylindrical geometry is presented in Bernales [2013].

\(^{27}\) But the Neumann boundary condition for the solute is still valid due to the flat concentration gradient at the impermeable wall (the same reason as in Equation 3.73).
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Figure 3.10: Algorithm implemented for solving the coupling of hydrodynamics and solute transfer numerically. $c_p^{(n+1)}$ is the local permeate concentration which will be covered in section 3.2.4. Adapted from Bernales [2013].
3.2.4 Numerical Modeling of the Coupling of Membrane Transport to Hydrodynamics and Bulk Mass Transfer

The developments brought to the previous model during this thesis intended to:

- Relax the hypothesis according to which the walls are completely impermeable to the solute even though they are permeable to the solvent, i.e., admit a solute flux across them and the consequences it brings about;
- Modify the expressions adopted for solvent and solute transport across the permeable wall in accordance with membrane transport mechanisms and models from the literature.

In other words, to couple problematics of “membrane transport” to the “hydrodynamic and bulk-mass-transfer” problem we have just seen [Lopes et al., 2014]. Keeping most of the considerations of the previous sections, the modifications pertain to the boundary conditions of the hydrodynamic and bulk-mass-transfer problems.

Figure 3.11 illustrates the new problem.

The mass balance on the surface of the permeable wall changes. Now, the solute carried by convection by the transverse fluid flow onto the wall surface is balanced by the retro-diffusion of solute into the bulk and by the transmembrane solute flow. Noting \( C_p(Z) \) the solute concentration in the permeate:

\[
U(d, Z)C(d, Z) = D_0 \frac{\partial C}{\partial X}(d, Z) + U(d, Z)C_p(z) \quad (3.140)
\]
A dimensionless value of permeate concentration, \( c_p(z) \), can be defined:

\[
c_p(z) = \frac{C_p(Z)}{C_{in}}
\]  

(3.141)

Different expressions for these and other parameters are obtained depending on the membrane transport model employed. We illustrate the general reasoning behind their determination and deduce here the corresponding formulae for solution-diffusion boundary conditions. The analogous development for Kedem-Katchalsky boundary conditions is presented in Appendix C.

### 3.2.4.1 Boundary Conditions for a Solution-Diffusion Membrane

The volumetric permeate flux and solute molar fluxes according to the solution-diffusion model are described by:

\[
J_v = I_0^{-1}(\Delta P - \Delta \pi)
\]
\[
J_s = B(\Delta C)
\]

We introduce the dimensionless solute permeability, \( \beta^* \). It may be understood as a ratio of the permeation velocities of the solute and of the solvent.

\[
\beta^* \equiv \frac{B}{U_{in}}
\]  

(3.142)

Table 3.5 summarizes the parameters of the new problem whose permeable walls are solution-diffusion membranes (as seen in section 2.1.2.4):

<table>
<thead>
<tr>
<th>Dimensional parameters</th>
<th>Dimensionless parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{in} ) ( C_{in} ) ( W_{in} ) ( d ) ( L ) ( I_0^{-1} ) ( B ) ( \rho_0 ) ( \mu_0 ) ( D_0 )</td>
<td>( Re_{in} ) ( Pe_{in} ) ( \alpha ) ( N_{osm} ) ( \tau ) ( \beta^* )</td>
</tr>
</tbody>
</table>

(3.35) \( (3.59) \) \( (3.38) \) \( (3.80) \) \( (3.37) \) \( (3.142) \)

Table 3.5: Ten dimensional and six dimensionless parameters describe the complete problem when a solution-diffusion mechanism is considered at the walls.

Writing the solute conservation across the membrane:

\[
B[C(d,Z) - C_p(Z)] = U(d,Z)C_p(z) \Rightarrow C_p(Z) = C(d,Z) \left[ \frac{B}{B + U(d,Z)} \right]
\]  

(3.143)

141
It follows in dimensionless form:

\[ c_p(z) = c(1, z) \left[ \frac{\beta^*}{\beta^* + u(1, z)} \right] \] (3.144)

In dimensionless form, the mass balance 3.140 on the wall surface results in a new boundary condition (which substitutes \((\partial c/\partial x) = u(1, z)c(1, z)Pe_{in}\) of Equation 3.86) is:

\[ \frac{\partial c}{\partial x}(1, z) = Pe_{in} u^2(1, z)c(1, z) \left[ \frac{1}{\beta^* + u(1, z)} \right] \] (3.145)

This condition is discretized and adapted to the form of Equation 3.109:

\[ c_{j+1}^{n+1} = c_{j-1}^{n+1} + 2\Delta x Pe_{in} \left[ \frac{\hat{u}_{j+1}^{n+1}}{\hat{u}_{j}^{n+1} + \beta^*} \right] c_{j}^{n+1} \] (3.146)

\[ B1(J) = Pe_{in} \left\{ \frac{3}{2\Delta z} \hat{w}_{0}^{(n+1)} - \frac{2}{\Delta x} \left[ \frac{\hat{u}_{j+1}^{n+1}}{\hat{u}_{j}^{n+1} + \beta^*} \right] \right\} + \frac{2}{(\Delta x)^2} \] (3.147)

The osmotic pressure of the permeate is non-zero and modifies the driving force for the permeation of solvent. The new condition of permeation (which substitutes \(u(1, z) = p(1, z) - N_{osm}c(1, z)\) of Equation 3.86) reads:

\[ u(1, z) = p(1, z) - N_{osm}[c(1, z) - c_p(z)] \] (3.148)

Its discretization and subsequent adaptation to the form of Equation 3.129 gives:

\[ \left( \frac{3\Delta x}{4\Delta z} \right) w_{0}^{(n+1)} + \left( \frac{3\Delta x}{2\Delta z} \right) \sum_{j=1}^{j=J-1} w_{j}^{(n+1)} + p^{(n+1)} = N_{osm} \left[ 1 - \frac{\beta^*}{\beta^* + \hat{u}_{j}^{(n+1)}} \right] c_{j}^{(n+1)} \] (3.149)

\[ R2(J) = N_{osm} \left[ 1 - \frac{\beta^*}{\beta^* + \hat{u}_{j}^{(n+1)}} \right] c_{j}^{(n+1)} + \frac{\Delta x}{2\Delta z} \left( 2w_{0}^{(n)} - \frac{1}{2}w_{0}^{(n-1)} \right) \] (3.150)

Other coefficients in matrixes 3.134 and 3.135 remain unaltered.
The new permeation velocity to be used in the convergence test is:

\[ U^{(k+1)} = p^{(n+1)} - N_{osm}C_j^{(n+1)} \left[ 1 - \frac{\beta^*}{\beta^* + u_j^{(n+1)}} \right] \]  

(3.151)

Problem solving follows as presented in the previous section according to the algorithm in Figure 3.10.

The analogous development admitting Kedem-Katchalsky boundary conditions is presented in Appendix C.

### 3.2.5 A Simulation Study

We show now some simulations in order to illustrate the capabilities of the numerical tool just presented and to highlight results and discussions of interest. First, some nomenclature is defined.

The dimensionless transverse velocity at the grid point(s) \((1, z)\) (or permeate flux), the membrane surface concentration at the same point(s) and the local permeate concentration are termed \(u_M, c_M\) and \(c_P\):

\[ u_M = u_j^{(n+1)} \]  

(3.152)

\[ c_M = c_j^{(n+1)} \]  

(3.153)

\[ c_P = c_p(c_M; u_M) = c_j^{(n+1)} \left[ \frac{\beta^*}{\beta^* + u_j^{(n+1)}} \right] \]  

(3.154)

The permeate flux and concentration averaged axially over the membrane length are \(u_{Mav}\) and \(c_{Pav}\). They help define the permeation Péclet number averaged over the membrane length, \(Pe_{av}\), and \(R_{av}\), the corresponding rejection rate taken in relation to the feed concentration (or “apparent” rejection rate):

\[ u_{Mav} = \frac{1}{(n+1)\Delta z} \sum_{n=0}^{n-N-1} \frac{u_j^{(n+1)} + u_j^{(n)}}{2} \Delta z \]  

(3.155)

\[ c_{Pav} = \left( \sum_{n=0}^{n-N-1} \frac{u_j^{(n+1)}c_j^{(n+1)} + u_j^{(n)}c_j^{(n)}}{2} \Delta z \right) / \left( \sum_{n=0}^{n-N-1} \frac{u_j^{(n+1)} + u_j^{(n)}}{2} \Delta z \right) \]  

(3.156)

\[ Pe_{av} = \frac{u_{Mav}d}{D_0} \]  

(3.157)

\[ R_{av} = 1 - c_{Pav} \]  

(3.158)
3.2.5.1 Outcomes of the Transmembrane Solute Flow

We raise the question of how sensitive the process outputs are to different solute and solvent permeability values. We first analyze a case typical of RO and afterwards a case typical of NF.

3.2.5.1.1 Reverse Osmosis

In this test case, a completely solute-rejecting membrane \((B = 0)\) and membranes whose permeabilities are lower and higher than the ones found for the RO membrane in Table 2.1 \((0[10^{-7} \text{ m} \cdot \text{s}^{-1} - 10^{-8} \text{ m} \cdot \text{s}^{-1}])\) are simulated for the desalination of water containing sodium chloride (solution assumed to follow van’t Hoff’s law) in a symmetric flow channel at 25°C; the range of permeability values comprises and exceeds the usual values of salt permeability for RO desalination membranes. A water permeability of \(5 \times 10^{-12} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}\) was chosen, a typical order of magnitude for RO desalination membranes in pressure-driven operation and in accordance with the values obtained with a RO membrane in Table 2.1. The channel half-height is set to \(d = 0.5 \text{ mm}\), in the order of magnitude of some industrial modules [Dow, b]. A long membrane of \(L = 6 \text{ m}\) is considered, as in a frequent industrial case in the desalination industry where up to 6 membranes of 1 m each may be arranged in series [Dow, e]. Feed concentrations from \(C_{in} = 1 \text{ g} \cdot \text{L}^{-1}\) up to \(C_{in} = 35 \text{ g} \cdot \text{L}^{-1}\) are considered (from a low-concentration brackish water up to standard seawater); applied pressures range from \(P_{in} = 1.5 \times 10^5 \text{ Pa}\) up to \(P_{in} = 60 \times 10^5 \text{ Pa}\); \(W_{in} = 0.1 \text{ m} \cdot \text{s}^{-1}\). In our simulations, the physical properties \(\rho_0\), \(\mu_0\) and \(D_0\) are given by linear laws [Geraldes et al., 2002]. The discrete domain contains 1000 transverse and 8000 axial grid points.

Figure 3.12 shows the permeate fluxes averaged over the entire membrane length for different conditions.

Some qualitative remarks on this graph are done. As the applied pressure \((P_{e_{in}})\) increases, so does the permeate flux \((P_{e_{av}})\), but not at same proportions because of the reduction of the effective driving pressure for permeation as a result of the osmotic counter-pressure: \(P_{e_{in}}\) goes up to 10, while \(P_{e_{av}}\) does not exceed 3. The plot is considerably linear for lowest feed concentration up to a condition of very high concentration polarization. As the feed concentration rises, the permeate flow is inflected at much lower pressures due to the reduction of the effective pressure difference when concentration polarization becomes severer. As previously
Figure 3.12: Diagram of 3 Péclet numbers for three concentrations and various values of solute permeability ($B$ or $\beta^*$).

seen, concentration polarization combined with osmosis implies a higher osmotic pressure difference.

The solute permeability $B$ exerts an influence on the permeate flux, which is seen to be higher for higher $B$, and whose causes we will examine soon. The differences are however slight: major enhancement in permeation exists only when the most solute-permeable – or less selective – membranes are simulated ($B = 10^{-7} \text{ m·s}^{-1}$ and $B = 10^{-6} \text{ m·s}^{-1}$) with the two more concentrated feeds. At higher pressure and $C_{in} = 1 \text{ g·L}^{-1}$, the limit flux (cf. 3.2.2) is approached and calculation time burgeons.

In the following, $z$ is the axial coordinate normalized by the channel length $L = 6 \text{ m}$. We pursue our analysis having Figure 3.13 as basis. When reading the graphs, remember that each concentration (color), velocity and pressure is nondimensionalized by its respective value in the feed. The specific effect of $B$ is explained after some comments on the qualitative effects seen on the graphs.

For negligible viscous pressure drop, the main factor modifying the permeate flux is the osmotic pressure difference across the membrane as shown in Figures 3.13c and 3.13d: the higher the osmotic gradient $N_{osm}(c_M - c_P)$, the lower the effective pressure difference, $p - N_{osm}(c_M - c_P)$, and, accordingly, the permeate flux. From Figures 3.13a and Figure 3.13b, the membrane surface concentration increases along the channel because the permeation of solvent naturally concentrates the
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(a) Local values of membrane surface and permeate concentrations for feeds of 10 g·L\(^{-1}\) and 35 g·L\(^{-1}\) at 60 \(\times\) \(10^5\) Pa.

(b) Local values of membrane surface and permeate concentrations for a feed of 1 g·L\(^{-1}\) at 1.5 \(\times\) \(10^5\) Pa.

(c) Axial evolution of the hydrodynamic pressure, osmotic pressure difference and permeate flux for feeds of 10 g·L\(^{-1}\) and 35 g·L\(^{-1}\) at 60 \(\times\) \(10^5\) Pa.

(d) Axial evolution of the hydrodynamic pressure, osmotic pressure difference and permeate flux for a feed of 1 g·L\(^{-1}\) at 1.5 \(\times\) \(10^5\) Pa.

Another observation is that from the Figure 3.13a. It reveals that, proportionally \(i.e.,\) in dimensionless form, the membrane surface concentration attains values much higher when the feed solution is less concentrated. What happens is that higher feed concentrations engender lower permeate fluxes because of higher osmotic counter-pressures, therefore engendering lower concentration polarization, \(i.e.,\) lower membrane surface concentration.

The osmotic gradient is reduced if the osmotic pressure on the retentate side is lowered and/or if the osmotic pressure of the permeate increases, so that both behaviors shall be evaluated. An obvious observation from Figures 3.13a and 3.13b is
that the local permeate concentration, $c_P$, is higher when the membrane is less selective. A (perhaps) less intuitive fact is that also $c_M$, the local membrane surface concentration, was higher in this case. Be that as it may, the local concentration difference across the membrane, $c_M - c_P$, is lower for a less selective membrane. As a consequence, the local osmotic counter-effect in Figures 3.13c and 3.13d, $N_{osm}(c_M - c_P)$, is lower for the situation of higher solute permeability. Given that the viscous pressure drop represented by the reduction of $p$ is equivalent for both permeability values, the higher permeate fluxes in Figure 3.12 for membranes of higher solute permeability are explained. As for the membrane surface concentration, higher permeate fluxes result in higher accumulation on the membrane surface, as seen on the graphs. Indeed, the diffusive transport of solute back to the bulk, even when combined with the permeation of solute (which is qualitatively too low in membrane separations), is not able to exceed the higher supply of solute, and the surface concentration rises in consequence.

We summarize the main “mechanisms” related to the effect of the solute permeability $B$ on the entire problem:

- Higher solute permeability results in higher permeate flux;
- The permeate flux is higher for higher $B$ because the osmotic pressure difference across the membrane is lower for higher $B$;
- The osmotic pressure difference across the membrane is lower for higher $B$ despite the fact that the membrane surface concentration is higher in this case. The increased permeate concentration with higher $B$ compensates the enhancement of the membrane surface concentration;
- Even if the effect is less pronounced, the higher permeate fluxes at higher $B$ result in lower pressure drop in the feed channel, what has, in turn, the effect of fostering the enhancement of the permeate flux compared to a situation of lower $B$.

We illustrated up to here axial gradients. We are now interested in evaluating the previous conclusions by examining transverse profiles at different points along the membrane. This is done with the examples of Figure 3.14. When reading the graphs, notice that the values for $B = 10^{-8}$ m·s$^{-1}$ practically coincide with those for $B = 0$.

All transverse profiles are appreciably different for $B = 10^{-6}$ m·s$^{-1}$ compared to $B = 10^{-8}$ m·s$^{-1}$ or $B = 0$, the two last cases being essentially equal. The differences
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Figure 3.14: Dimensionless transverse profiles at different positions $z$ along the membrane for a feed of $10 \text{ g.L}^{-1}$ at $30 \times 10^5 \text{ Pa}$ considering three values of $B$. Values for $B = 10^{-8} \text{ m.s}^{-1}$ practically coincide with those for $B = 0$.

are accentuated in the zone adjacent to the membrane so that the transverse gradients of concentration (Figure 3.14a) and transverse velocity (Figure 3.14b) are at all points steeper for higher solute permeability. Actually, the higher transverse velocity for higher $B$ explains the enhanced values of $c_M$ found in Figures 3.13a and 3.13b for higher $B$, because the transverse velocity is directly related to the permeate flux (they are equal on the membrane surface). The increased momentum transfer by $u$ at higher $B$ is reflected in the lower values of $w$ (Figure 3.14c) what, in turn, sweeps solute downstream in the sheared zone less effectively (therefore not contributing to the reduction of the polarization layer). Therefore, as everything is coupled, not only the permeate but also the retentate is sensibly affected by $B$: 
The retentate is slowed down, its flow rate decreases and it gets more concentrated. The focus of most separations is to purify the permeate. Nevertheless, sometimes one is interested in concentrating the feed stream: in such cases, a less selective membrane of higher solute permeability can be a good choice.

The transverse gradients of the velocities, limited indirectly by fixed-value boundary conditions at $x = 0$, are significantly reduced as the axial coordinate increases: $u$ as a result of the increasing polarization effect detrimental to the permeation of solvent, and $w$ as a result of the deceleration of the retentate consequent to the reduction of the flow rate in the flow channel (of fixed dimensions). The axial evolution of the concentration gradient is such that it resembles less and less a film-type profile. Also $c(x = 0)$ grows, almost doubling along the channel. Actually, the whole bulk becomes more concentrated as it flows owing to the loss of solvent through permeation: in fact, the retentate exits the flow channel more concentrated than all other streams and slower than the feed.

The permeate concentration is much more sensitive to $B$ (and, unsurprisingly, higher for higher solute permeabilities) as illustrated by Figure 3.15. It is very interesting to note that the permeate concentration has a non-monotonic dependence on the applied pressure ($P_{ein}$), that it reaches a minimum value whose position in relation to the abscissa axis moves somewhat to the right.

![Figure 3.15](image)

Figure 3.15: Averaged permeate concentration obtained for various $P_{ein}$ and values of solute permeability ($B$ or $\beta^*$) with three concentrations. The permeate concentration has a non-monotonic dependence on the applied pressure, such that a minimum is identified. Negative rejections are attained depending on the operating conditions.
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We propose to analyze it in Figure 3.16 for $C_{in} = 10 \text{ g} \cdot \text{L}^{-1}$ and $P_{in} = 60 \times 10^5 \text{ Pa}$. As the solute permeability is increased, the enhancement of solvent permeation turns out to be insufficient for diluting the increasing part of the salt flux. As a matter of fact, the dimensionless solute molar flux, $u_Mc_P$, is locally directly proportional to the solute permeability value, whereas the dependence of the permeate flux on $B$ is indirect and, as previously assessed, much more attenuated.

![Figure 3.16: Axial evolution of the dimensionless solute and permeate fluxes for a feed of 10g L$^{-1}$ at 60 × 10$^5$ Pa for different B.](image)

Figure 3.16: Axial evolution of the dimensionless solute and permeate fluxes for a feed of $10 \text{ g} \cdot \text{L}^{-1}$ at $60 \times 10^5 \text{ Pa}$ for different $B$.

We mean that a trade-off dependent on the inlet pressure exists between permeate flux and solute flux, and defines two regimes for which, alternately, one of the fluxes is preponderant over the permeate concentration: the dilutive regime at lower pressures, and concentrative regime at higher pressure. In the first case, the applied pressure results in a proportionally higher permeate flux; in the second case, concentration polarization is severer, the permeate flux drops and the solute flux rises. In other terms, the rejection rate reaches a maximum, after which operation at higher pressure will result in lower or even negative rejection.

Figures 3.13 and 3.14 already pointed out that important quantitative differences exist when most parameters are evaluated at different positions in the axial direction. Figures 3.17a and 3.17b illustrated values averaged since the channel entrance and up to $z$, and are aimed at solely emphasizing that not only local values but also the two main process results, the averaged (“accumulated”) permeate flux and concentration (or rejection rate), will vary drastically if membranes of different lengths $z$ are employed. Being able to simulate such variations is a decided
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plus of local models.

\[ (a) \ C_{in} = 10 \text{ g} \cdot \text{L}^{-1}. \]

\[ (b) \ C_{in} = 35 \text{ g} \cdot \text{L}^{-1}. \]

Figure 3.17: Averaged dimensionless permeate flux and concentration up to the axial position \( z \) for \( B = 10^{-6} \text{ m} \cdot \text{s}^{-1}, P_{in} = 60 \times 10^5 \text{ Pa} \) and a total length of \( L = 6 \text{ m} \).

The previous results show that, in principle, membrane selectivity affects the coupling between hydrodynamics and mass transfer in the feed channel by, primarily, modifying the fluid velocity normal to the membrane, thereby determining the extent of concentration polarization. However, the changes are negligible unless the solute permeability increases of too many orders of magnitude. Therefore, within narrower ranges of solute permeability more representative of individual processes, it seems appropriate to evaluate the permeate flux separately from its concentration. This is an opportune “rule of thumb”. Nevertheless, membrane selectivity is a parameter upon which the rejection rate is significantly sensitive. This points out the need for adequate membrane transport parameters in order to achieve a complete and accurate prediction of process performance.

The solute permeability values simulated covered six orders of magnitude. In reality, the permeability values characteristic of each process (RO, NF etc.) for electrolyte separations are much more limited: physically, excessive changes in solute passage are typically accompanied by concurrent changes in solvent permeation. The membrane structure is modified and, accordingly the transport mechanisms.

It is worth reminding that the permeability of a membrane is not a universal property because its value also depends on the solvents and solutes (and on the operating parameters) to which the membrane is exposed during the filtration process. Certain selectivity values, when combined with appropriate operating conditions, engender the occurrence of negative rejections (permeate more concentrated than the feed) [Yaroshchuk, 2008], a possibility verified in Figure 3.15.
for the most dilute solution with the most solute-permeable membrane at higher operating pressures.

The cases here simulated also highlight that the use/development of membranes of too low solute permeability (here below $B \sim 10^{-8} \text{ m} \cdot \text{s}^{-1}$) is not utterly advantageous in many applications because the rejection rate is not significantly enhanced regardless of the operating conditions. These “subtle” enhancements are however significant for several applications in RO which require rejections more and more elevated (e.g. above 99.5% in the medical-sanitary field), raising the question of how far predictive simulation tools like the one of this thesis can go, for the time being, in the determination of the permeate concentration for the latter applications given that, for the time being, they still cannot be “supplied” with membrane transport parameters as fine as would need such limit applications.

At the other end of the permeability scale, it is possible to conclude from the results that the permeate flux and concentration are more sensitive to the solute permeability in the range of higher $B$ (here above $B \sim 10^{-8} \text{ m} \cdot \text{s}^{-1}$). We could therefore expect the prediction of process performance for applications in this range of values to be more complicated and, again, the need for accurate membrane transport parameters to be proportionally more elevated – even before introducing transport parameters which account for convection or other transport mechanisms.

### 3.2.5.1.2 Nanofiltration

We analyzed a case typical of RO so far. We would like now to get the measure of these effects for a solution-diffusion membrane of much higher solvent permeability in pressure-driven mode, typical of NF membranes as that in Table 2.1. A membrane for which $L = 1 \text{ m}$ and $I_0^{-1} = 5 \times 10^{-11} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ is therefore considered. Like before, $d = 0.5 \text{ mm}$ and $T = 25^\circ \text{C}$, $C_{in} = 5 \text{ g} \cdot \text{L}^{-1}$ (NaCl in water following van’t Hoff law) (in dimensionless form, this corresponds to a constant $N_{osm}$), $P_{in} = 22.5 \times 10^5 \text{ Pa}$ and $W_{in} = 0.1 \text{ m} \cdot \text{s}^{-1}$. The results are compared with those obtained with a membrane of $I_0^{-1} = 5 \times 10^{-12} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ (all other parameters being kept equal).

Notice that Prandtl’s approximations (sections 3.2.1.2 and 3.2.2) still hold even if the permeation velocity (e.g. $U_{in}$) is increased of approximately one order of magnitude. Now, the reduced membrane solvent permeability (Equation 3.39) is of order $\beta \sim 10^{-11} - 10^{-10}$; in the previous analyses, it was of order $\beta \sim 10^{-12} - 10^{-11}$. In both cases, $\alpha^2 \sim 10^{-3} - 10^{-1}$, so that $\beta/\alpha^2 \longrightarrow 0$ (or $[U_{in}/W_{in}]^2 \ll 1$).
Figure 3.18 indicates how the averaged dimensionless permeate flux and rejection rate vary with the axial coordinate (or membrane length) for different values of solvent and solute permeability.

![Diagram](image)

(a) Axial evolution of the averaged permeate flux. (b) Axial evolution of the averaged rejection rate (in relation to the feed concentration).

Figure 3.18: Axial evolution of the averaged dimensionless permeate flux and of the rejection rate for $C_{in} = 5 \text{ g L}^{-1}$, $P_{in} = 22.5 \times 10^5 \text{ Pa}$ and a total membrane length of $L = 1 \text{ m}$ for different solvent and solute permeabilities, $I^{-1}$ and $B$.

First of all, the tenfold enhancement of $I^{-1}$ (or $Pe_{in}$) is not reflected in $Pe_{av}$, which is markedly lower (two- to sevenfold), suggesting very intense concentration polarization. The rejection rate is not completely modified between membranes of so different solvent permeability. Again, the permeate flux and the rejection rate vary only very little with the solute permeability value, except for the highest $B$. We will come back to the rejection values soon.

When reading the coming graphs in Figure 3.19, notice that the values for $B = 10^{-8} \text{ m s}^{-1}$ practically coincide with those for $B = 0$. Figures 3.19a and 3.19b reveal that, indeed, the dimensionless concentrations in the feed channel limited by the more solvent-permeable membranes can be more than two times those with the less permeable membrane close to the membrane. The former concentration profile is clearly steeper. As seen in Figures 3.19c and 3.19d, the enhanced polarization concurs with a much flatter transverse profile for the transverse velocity, whose dimensionless values are at some points lower than $1/6$ of those calculated for lower $I^{-1}$.

These analyses showed that concentration polarization is proportionally much more intense with the more permeable NF membrane than with the RO one. We return to rejection values in Figure 3.18. For highest $B$, and if the membrane
CHAPTER 3. Modeling of Hydrodynamics and Bulk Mass Transfer in Membrane Processes

(a) Transverse concentration profile for $I_0^{-1} = 5 \times 10^{-11} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$.

(b) Transverse concentration profile for $I_0^{-1} = 5 \times 10^{-12} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$.

(c) Transverse profile of the transverse velocity for $I_0^{-1} = 5 \times 10^{-11} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$.

(d) Transverse profile of the transverse velocity for $I_0^{-1} = 5 \times 10^{-12} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$.

Figure 3.19: Dimensionless transverse profiles at different positions $z$ along the membrane for a feed of $5 \text{g} \cdot \text{L}^{-1}$ at $22.5 \times 10^5 \text{Pa}$ considering three values of $B$. Values for $B = 10^{-8} \text{m} \cdot \text{s}^{-1}$ practically coincide with those for $B = 0$. $c$ is normalized by the feed concentration as usual.

length is in reality enough for it, the rejections of the NF and RO membrane intersect each other and that of the NF membrane starts to be lower than the RO one. The proportionally more critical drop of permeate flux for higher $I_0^{-1}$ conjugated with a near-constant solute flux along the membrane for highest $B$ explains the lower rejection seen before for highest $I_0^{-1}$ and $B$ (a comparative between RO and NF of the two “regimes” previously seen). This is depicted in Figure 3.20.

This numerical code was compared to the analytical solutions seen in the previous sections as references, as well as to some models and results from the literature [Bernales, 2013; Bernales et al.]. Among others, an important conclusion (supported by the simulations we have just presented) was that, in our model, the
Figure 3.20: Axial evolution of the dimensionless solute and permeate fluxes for a feed of 5 g·L$^{-1}$ at 22×10$^5$ Pa for different $I_0^{-1}$ and $B$.

permeate flux undergoes a significant decay in the initial region of the flow channel due to the development of an important concentration polarization layer already in this zone.

### 3.3 Chapter Conclusion

Modeling pressure-driven membrane separations cannot circumvent the description of concentration polarization because the latter determines, to a very large extent, the behavior and outputs of the process for given operating conditions and membrane characteristics. This study is tantamount to modeling the simultaneous and interdependent momentum and mass transports taking place in the cross-flow.

The task can be undertaken by simplified phenomenological models which resort to averaged descriptions of, admittedly, pertinent parameters (e.g. permeate flux and osmotic pressure). If they are capable of describing specific results and applications, they are neither predictive nor general. Their limitations stem basically from the oversimplification of the hydrodynamics in the feed channel (specially from considering an unsheared concentration boundary layer), from the neglect of the axial variation of driving forces and outputs and from the dependence upon parameters of difficult measurement (e.g. split of mass transfer resistances) or of high application-specificity (e.g. mass transfer coefficients).
“Second-level” approaches describe the main process variables locally. They can be more complex mathematically but have superior accuracy and comprehensiveness. A multitude of approaches exist.

We presented a local, first-principles approach of increasing complexity and representativeness (as compared to standard applications) which relies on reduced sets of input parameters, for the most part known by the experimentalist in advance or of unchallenging determination. The rationalization of the problem by means of a few dimensionless parameters enabled to ally physical realism with a somewhat simpler mathematical treatment (including Prandtl hypotheses). Within their limits, the analytical and numerical models derived from this approach have the advantageous feature of not requiring heuristic considerations for determining the physical behavior of the system: the parameters and equations explain the process evolution by themselves.

The current state of the numerical model couples membrane transport to the hydrodynamic and bulk-mass-transfer problems. From a modeling perspective, this corresponds to the modification of boundary conditions of the model. From the experimental point of view, the main difficulty is the determination of the membrane transport parameters, more precisely of those pertaining to the solute transfer.

Precisely at the membrane surface, a very subtle coupling between hydrodynamics, concentration polarization, axial pressure drop and membrane transport properties takes place. These parameters are for the most part dependent on each other and should ideally be treated together, simultaneously, in order to achieve accurate and comprehensive prediction of the various process outputs (permeate and retentate). Membrane design and process design performed based only on hydrodynamic considerations are not the optimum.

A simulation study demonstrated that the solute permeability is a parameter whose influence appears in principle on both membrane sides: it affects the permeate flux and its composition whilst modifying the cross-flow and the mass transfer on the retentate side, and the final condition of the retentate itself as a consequence. Mass transfer across the membrane and in the feed channel are essential. That said, we could say that it is possible to separate the determination of the permeate flux from that of the permeate concentration in many cases if the membrane is highly selective. A turning point for the solute permeability $B$ can be discerned around $10^{-8}$ m·s$^{-1}$. The assumption of total rejection is adequate below this point.
as far as the permeate flux is concerned (what is already a very important milestone) because, for practical purposes, the permeate flux is only sensitive to the hydrodynamic conditions leading to concentration polarization, conditions which are almost not modified by $B$ below this point. On the other hand, the rejection rate is influenced chiefly by the solute permeability value, even though it is not independent from the conditions on the feed channel— not to mention the dependence of the membrane transport parameters upon concentration and pressure as discussed in Chapter 2. This “uncoupled” treatment of the problem becomes less valid as the membrane selectivity decreases, calling for a better knowledge of the membrane transport parameters. Naturally, the accuracy expected for the model’s predictions in all cases is a matter of discussion.

The numerical model may be envisioned at this point as a tool for process simulation and design since it determines, among others, two of the most important process parameters: the permeate flow rate and its concentration. Before, the model needs to be validated. This is the subject of the next Chapter, in which the model’s predictions are compared to results from the literature and to own experiments. At the appropriate time, the analyses and results of Chapter 2 will be incorporated to our discussions.
CHAPTER 4

Model Validation and Comparison to Experiments

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This Chapter is essentially applied and experimental. It is dedicated to two big objectives which we present below.

The first one is to compare our numerical simulations with experimental results. This validation is done by comparing the numerical predictions with data from the literature and with our own experiments. In the first case, data from five publications are used. Four of them concern reverse osmosis and nanofiltration separations carried out in laboratory-scale plate-and-frame modules.
CHAPTER 4. Model Validation and Comparison to Experiments

The fifth case is that of a long spiral-wound membrane module. For this reason, an overview of problematics pertaining to spacer-filled channels and spiral-wound modules is presented. The particular modeling and simulation approach based on the concept of hydraulic dispersion coefficients or apparent Schmidt numbers will be presented at this moment. Our experiments with spiral-wound membranes are simulated in light of this approach. They concern mainly RO but a brief insight into NF is also provided.

The second purpose of this Chapter is to evaluate the adequacy of the solute permeability coefficients determined in Chapter 2 during osmotic-diffusive experiments for the simulation of pressure-driven separations (reverse osmosis). A discussion of this question is presented.

The Chapter is closed with concluding remarks.
CHAPTER 4. Model Validation and Comparison to Experiments

4.1 Comparison with Data from the Literature

In this section, we compare the results of our numerical simulations with experimental and semi-experimental data reported in the literature with either reverse osmosis or highly rejecting nanofiltration membranes. The great difficulty here is to find publications containing all the physical input parameters required by our model or at least information from which they can be deduced.

Five studies are presented. Plate-and-frame and spiral-wound modules are considered because they correspond to a two-dimensional geometry. The asymmetric and symmetric versions of the numerical code are employed according to the geometry.

The following notation will be useful. The dimensional permeate flux averaged axially, the intrinsic rejection (calculated in relation to the membrane surface concentration instead of to the feed concentration) and the membrane surface concentration averaged axially are, respectively:

\[
U_{av} = u_{Mav}U_{in} \tag{4.1}
\]

\[
P_{int}^{av} = 1 - \frac{c_{P}^{av}}{c_{M}^{av}} = 1 - \frac{1}{(n+1)} \sum_{n=0}^{n=N-1} \frac{1}{(n+1)} \sum_{n=0}^{n=N-1} c_{J}^{(n)} \tag{4.2}
\]

\[
C_{M} = c_{M}C_{in} \tag{4.3}
\]

4.1.1 Case I

Ahmad and Lau [2007] treated aqueous solutions of sucrose, of MgSO\textsubscript{4} and of Na\textsubscript{2}SO\textsubscript{4} with the flat-sheet polyamide TFC nanofiltration membrane NF90 (Dow Filmtec) installed in an asymmetric channel (that is, limited by one impermeable wall). The effective filtration zone measured 25.5 cm × 2.5 cm × 0.1 cm (lenght \(L\) × width \(w_{l}\) × channel full-height \(d\)). For each substance, one feed concentration \(C_{in}\) was tested for two axial \(Re\) (from Equation 3.6) or velocities \(W_{in}\) for each of the five values of inlet pressure \(P_{in}\) at \(T = 25^\circ\text{C}\) (values in Table 4.1). The membrane water permeability is given as \(I_{0}^{-1} = 4.72 \times 10^{-11} \text{m⋅Pa}^{-1}\text{⋅s}^{-1}\). The physical properties \(\rho_{0}, \mu_{0}\) and \(D_{0}\) are given by polynomial or power laws of the solute concentration, so do the osmotic pressures [Ahmad and Lau, 2007]. Solute permeability and reflection coefficients were estimated by the authors by fitting the intrinsic rejection (thereby accounting for the effect of concentration polarization) and permeate flux values within an iterative calculation loop containing
CFD simulations of the flow and mass transfer in the feed channel to Equation 2.19 (sc. $F_{sc}/l$), which describes the rejection rate in the Spiegler-Kedem model. The reflection coefficients were all high and therefore neglected in our simulations ($\sigma_{\text{sucrose}} = 0.9994$, $\sigma_{\text{Na}_2\text{SO}_4} = 0.9945$ and $\sigma_{\text{MgSO}_4} = 0.9627$), which consider the solution-diffusion model. The solute permeability values given by the authors are: $B_{\text{sucrose}} = 1.0881 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$, $B_{\text{Na}_2\text{SO}_4} = 1.7526 \times 10^{-8} \text{m} \cdot \text{s}^{-1}$ and $B_{\text{MgSO}_4} = 4.3359 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$.

In the following, for $Re$ between 280 and 360, $W_{in}$ is comprised between 0.25 m·s$^{-1}$ and 0.33 m·s$^{-1}$. For $Re$ between 900 and 1900, $W_{in}$ is comprised between 0.82 m·s$^{-1}$ and 1.73 m·s$^{-1}$. We made the correspondence between the axial Reynolds number $Re$ provided by the authors for each experimental condition and $W_{in}$ by using the hydraulic diameter $d_h$:

$$d_h = 2 \frac{w_l d}{w_l + d} \quad (4.4)$$

The simulated values of permeate fluxes (“sim.”) are compared to the experimental ones (“lit.”) in Table 4.1 and illustrated in Figure 4.1. In the same Figure are also illustrated the simulated intrinsic rejection rates. Since the authors do not specify the conditions for which they calculated the latter values, we present them together with our calculated values obtained with the same simulations from which the values of permeate flux were calculated.

From Figure 4.1, we see that a good agreement exists between our predictions and the experiments, both for the permeate flux as well as for the rejection rates. Notice that the ordinate axis has a very narrow scale in two cases, superior to 0.99, so that our results are very pertinent. The form of the plots is always reproduced by our model.

From Table 4.1, the permeate fluxes are predicted within $\pm 15\%$ for most conditions, great part of them even within $\pm 8\%$. Only five out of thirty simulations deviate more than $15\%$ from the experimental values, all of them at lowest pressure. The water permeability value provided by the authors being, according to them, the average of experiments at five pressure values, the deviations could be due to some modification of the membrane permeability at different pressure ranges (perhaps in a similar way to what we verified during the conditioning process in Figure 2.4).

The effect of the axial velocity on the concentration polarization layer is correctly reproduced by the simulations. In Figure 4.1, the permeate fluxes are sensibly
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<th>Solute</th>
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<th>$Re_{in}$</th>
<th>$U_{av}$ (sim.) (m·s$^{-1}$)</th>
<th>$U_{av}$ (exp.) (m·s$^{-1}$)</th>
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Table 4.1: Comparison between experimental values of permeate flux, $U_{av}$, from Ahmad and Lau [2007] and from our simulations. Relative errors are calculated having the experimental values as references.
CHAPTER 4. Model Validation and Comparison to Experiments

Figure 4.1: Comparisons between experimental values of permeate flux, $U_{av}$, and of semi-experimental values of intrinsic rejection rate, $R_{av}^{int}$, from Ahmad and Lau [2007] and simulation results.
lower for lower $Re$, indicating higher concentrations on the membrane surface for these cases. It is possible to notice moreover an inflection as pressure is increased, even if the applied $Re$ is increased too, what demonstrates the preponderant effect of the transverse velocity (directly related to the permeation velocity). This trend has already been pointed out, in another context, by the diagram of “3 Péclet numbers” 3.7. The inflection is less marked with the sodium sulphate solution. Indeed, owing to a much higher diffusion coefficient of the solute in the bulk (i.e., retro-diffusion), the Schmidt number (Equation 3.7) for this solution, 779, is lower than for the magnesium sulphate and sucrose ones, 1460 and 1724 respectively.

The intrinsic rejection rates for sucrose and Na$_2$SO$_4$ are both very high, near to one. As discussed in section 3.2.5 of the previous Chapter, the accuracy of our model for such purposes is strongly dependent on that of the membrane transport parameters, which the authors have in turn estimated by means of a numerical model in the framework of a semi-empirical approach. Despite these considerations, we verify that our predictions are well close to the authors’ estimations. Neglecting the very high reflection coefficients was not detrimental to the predictions in these cases. However, for the salt with the highest permeability and reflection coefficient, MgSO$_4$, $R_{av}$ spanned a broad range of values between 0.90 and 0.97. In this case, we simulate values which exceed the authors’ ones in more than 0.02 when considering a pure solution-diffusion mechanism. In all cases, the form of the plots is reproduced by our simulations.

4.1.2 Case II

Zhou and Song [2005] treated aqueous solutions of NaCl with the flat-sheet reverse osmosis membrane CE (Osmonics) installed in an asymmetric channel (that is, limited by one impermeable wall). The effective filtration zone measured 19.1 cm $\times$ 14.0 cm $\times$ 0.171 cm (lenght $L$ $\times$ width $w_l$ $\times$ channel full-height $d$). Six feed concentrations $C_{in}$ were tested at nine applied pressures and one velocity $W_{in} = 0.28$ m$\cdot$s$^{-1}$ (or $Re = 373$ approx.) at constant “room temperature”, here considered $T = 20^\circ$C. The membrane water permeability can be deduced from one of the graphs, $I_0^{-1} = 4.26 \times 10^{-12}$ m$\cdot$Pa$^{-1}$s$^{-1}$. In our simulations, the physical properties $\rho_0$, $\mu_0$ and $D_0$ are given by linear laws [Geraldes et al., 2002] and the osmotic pressure is calculated with the van’t Hoff law. Solute permeability coefficients were estimated by the authors by calculating the linear regression of the reciprocals of the apparent rejection (thereby neglecting the ef-
fect of concentration polarization) and permeate flux values to a linear form of
the solution-diffusion (as in Equation 2.43 with $R_\infty = 1$). The solute perme-
ability values they found are concentration-dependent, their values for each $C_{in}$
being:

\begin{align*}
B_{0.1 \text{g} \cdot \text{L}^{-1}} & = 1.24 \times 10^{-7} \text{m} \cdot \text{s}^{-1}, \\
B_{0.5 \text{g} \cdot \text{L}^{-1}} & = 1.90 \times 10^{-7} \text{m} \cdot \text{s}^{-1}, \\
B_{1 \text{g} \cdot \text{L}^{-1}} & = 2.25 \times 10^{-7} \text{m} \cdot \text{s}^{-1}, \\
B_{5 \text{g} \cdot \text{L}^{-1}} & = 1.26 \times 10^{-7} \text{m} \cdot \text{s}^{-1}, \\
B_{10 \text{g} \cdot \text{L}^{-1}} & = 1.07 \times 10^{-7} \text{m} \cdot \text{s}^{-1} \text{ and} \\
B_{20 \text{g} \cdot \text{L}^{-1}} & = 5.56 \times 10^{-8} \text{m} \cdot \text{s}^{-1}.
\end{align*}

The coefficients of determination of the linear re-
gressions are bad, varying between 0.7935 ($B_{0.5 \text{g} \cdot \text{L}^{-1}}$) and 0.9235 ($B_{1 \text{g} \cdot \text{L}^{-1}}$). We
believe this is due to the neglect of concentration polarization by considering ap-
parent rejections instead of intrinsic rejection values.

For the permeate flux, a good qualitative agreement exists between simulations
and experimental values. For the rejection rates, only at low concentrations.

The comparison of experimental and simulated rejection rates in Figure 4.2 is very
good for the three least concentrated feeds and bad for the others. The model pre-
dicts values of rejection rate which are in most cases higher than the experimental
ones; the agreement becomes worse at low- and mid-range operating pressures.
This indicates that the solute permeability values are not appropriate. Errors in-
crease for the simulations at higher concentrations because these are the conditions
for which the salt flux, which is directly related to the solute permeability value,
has an even larger (concentrating) effect on the permeate concentration than does
that (diluting) of the water flux. In their study, the authors propose a modified
form of transport equations: the transmembrane water flux is given by a relation
similar to the one of the Kedem-Katchalsky model (Equation 2.15) but replacing $\sigma$
with the values of apparent rejection (the previous water permeability will change),
and the solute flux by “speculating” that it might be proportional (through a solute
permeability coefficient) to the concentration difference between the feed and the
permeate to a power greater than one. Briefly, the problem is modeled with feed
and bulk properties only, without resorting to any kind of quantitative description
of concentration polarization. As we have discussed in Chapter 2, this approach
is not advisable.

The simulated permeate fluxes are underestimated for the two highest concentra-
tions, with values between $\pm 15\%$–$\pm 27\%$ lower than the experimental ones for
$20 \text{g} \cdot \text{L}^{-1}$ and between $\pm 3\%$–$\pm 11\%$ for $10 \text{g} \cdot \text{L}^{-1}$. As $C_{in}$ diminishes, so do the
errors in the predictions, which furthermore inverse the previous tendency and
become overestimated.

The variation of the solute permeability coefficient is not capable of explaining
Figure 4.2: Comparisons between experimental values of permeate flux, $U_{av}$, and of apparent rejection rate, $R_{av}$, from Zhou and Song [2005] and simulation results.
these differences, even more so because the errors in the prediction of rejection rates proved to be frequently uncorrelated to those of the permeate flux. For illustration, Figure 4.3 presents the estimated permeate flux and rejection rates for $C_m = 20 \text{g} \cdot \text{L}^{-1}$ using a solute permeability value 10 times higher ($B = 5.56 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$) than the one indicated by the authors. As is seen, the rejection rates change completely, the magnitudes of the errors associated to their prediction increase but those associated to the permeate flux do not change enough (on top of that, some permeate change from underestimated to overestimated).

![Figure 4.3: Comparison of $U_{av}$ and $R_{int}$.](image)

The hypothesis according to which the water flux would be proportional to $\Delta P - \sigma \Delta \pi$ with $\sigma$ considerably different from unity, rather than to simply $\Delta P - \sigma \Delta \pi$, does not seem to be applicable here, at least not for constant $\sigma$, because the simulated permeate fluxes are not only underestimated but also overestimated depending on the conditions.

The authors in Zhou and Song [2005] mention that some permeate flux existed even for driving pressures lower than the osmotic pressure values and that this water flux “increased slowly and nonlinearly” as the operating pressure was augmented, but do not have an explanation for this occurrence. This could be explained by a reflection coefficient $\sigma$ different from unity. If $\sigma$ in this experiment is considerably different from unity, our overestimated permeate fluxes could be explained, but this is not a general explanation for all the deviations to the simulated values.
4.1.3 Case III

Salcedo-Díaz et al. [2014] carried out experiments aimed at visualizing the concentration polarization layer on the membrane surface under the form of concentration-dependent interference fringe patterns by using an optical technique called Digital Holographic Interferometry. The optical system was coupled to a plate-and-frame module whose filtration channel measured $22.0 \text{ cm} \times 1.5 \text{ cm} \times 0.43 \text{ cm}$ (length $L$ × width $w_l$ × channel full-height $d$) and possessed four observation windows at fixed distances from the entrance of the membrane module: 3 cm, 8 cm, 14 cm and 19 cm. Aqueous solutions of Na$_2$SO$_4$ of 3 kg·m$^{-3}$, 6 kg·m$^{-3}$ and 9 kg·m$^{-3}$ were analyzed at an operating pressure of $6 \times 10^5$ Pa by applying three values of $W_m$, 0.2 cm·s$^{-1}$, 0.7 cm·s$^{-1}$ and 2 cm·s$^{-1}$. The latter correspond to longitudinal Reynolds number of approximately 10, 35 and 100 respectively. The reverse osmosis membrane XLE-2540 (Dow Filmtec) was employed; a mean value $I_{10} = 1.29 \times 10^{-11}$ m·Pa$^{-1}$·s$^{-1}$ is reported. No information on the membrane solute permeability is provided or used in their study, even though the permeate concentration (conductivity) is monitored in order to ensure steady-state operation. In our simulations, we considered total rejection ($B = 0$). $\rho_0$, $D_0$ and the osmotic pressures were calculated with the relations presented by the authors; $\mu_0$ was calculated with the expression reported in Geraldes et al. [2002].

Table 4.2 synthesizes the membrane surface concentrations $C_M$ calculated by our model and those estimated optically for the solution of concentration 6 kg·m$^{-3}$.

The experimental values are all lower than the numerical predictions. The errors are much higher near to the entrance and to the exit of the flow channel, $Z = 3$ cm and $Z = 19$ cm. They also increase with $Re$. Furthermore, the experimental values of $C_M$ at $Z = 19$ cm are lower than at lower $Z$-values. As pointed out by the authors, edge effects, intensified by the previous conditions, could underlie these behaviors. In the middle of the channel, the local profiles would be more established, reflecting in the lower errors found at intermediate positions.

Table 4.3 compares the experimental and simulated permeate fluxes for this and other concentrations. In most cases, $C_{in} = 9$ kg·m$^{-3}$ included, the simulations of $U_{av}$ are underestimated. At lowest concentration, the model predictions are accurate within $\pm 5\%$. The errors are markedly higher for the two other concentrations, specially for 9 kg·m$^{-3}$; in these cases, they are a little more elevated when lower feed velocities are used. These remarks indicate that the experiments undergo
CHAPTER 4. Model Validation and Comparison to Experiments

Table 4.2: Comparison between experimental values [Salcedo-Díaz et al., 2014] of membrane surface concentration $C_M$ at different axial coordinates $Z$ and simulated values for $C_{in} = 6 \text{ kg} \cdot \text{m}^{-3}$. Relative errors are calculated having the experimental values as references.

<table>
<thead>
<tr>
<th>$Re$</th>
<th>$Z$ (cm)</th>
<th>$C_M$ (sim.) (kg$\cdot$m$^{-3}$)</th>
<th>$C_M$ (exp.) (kg$\cdot$m$^{-3}$)</th>
<th>Error $C_M$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3</td>
<td>9.49</td>
<td>7.82</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>9.94</td>
<td>9.38</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>10.16</td>
<td>9.94</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>10.27</td>
<td>8.83</td>
<td>16.3</td>
</tr>
<tr>
<td>35</td>
<td>3</td>
<td>8.85</td>
<td>6.91</td>
<td>28.1</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>9.35</td>
<td>8.58</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>9.62</td>
<td>8.63</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>9.77</td>
<td>8.02</td>
<td>21.8</td>
</tr>
<tr>
<td>100</td>
<td>3</td>
<td>8.30</td>
<td>6.61</td>
<td>25.6</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>8.81</td>
<td>7.46</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>9.10</td>
<td>7.52</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>9.26</td>
<td>6.81</td>
<td>36.0</td>
</tr>
</tbody>
</table>

Weaker concentration polarization and could point into the explanation of edge effects previously evoked, at least for $C_{in} = 6 \text{ kg} \cdot \text{m}^{-3}$.

Actually, from Figures 4.4a and 4.4b, the concentration profiles measured experimentally (only one point shown) are above the simulated ones in most of the flow channel for $C_{in} = 9 \text{ kg} \cdot \text{m}^{-3}$ and $Re = 10$, but below the simulations for $Re = 100$ and the same feed concentration. Even if this can be in line with the argument of higher edge effects at higher feed velocities, it does not explain why the experimental permeate fluxes are higher than the simulated ones even though the experimental polarization is higher.

The experimental module used by the authors is not a two-dimensional channel like the one of our model. In fact, their module measured $22.0 \text{ cm} \times 1.5 \text{ cm} \times 0.43 \text{ cm}$, so that the width is only 3.5 times bigger than the channel height. In addition to the geometrical differences between experiences and model, we believe that effects related to the proximity of the walls and to their big dimensions could have some influence on the relative errors that we found. Qualitatively speaking, we saw in section 3.2.2 that the Sherwood number characteristic of Green flow, which is confined by more walls than the Berman configuration, is 20% higher.
Table 4.3: Comparison between experimental values of permeate flux, $U_{av}$, from Salcedo-Díaz et al. [2014] and from our simulations. Relative errors are calculated having the experimental values as references.

than Berman’s Sherwood number. Since our simulations result most of the time in underestimations, and the authors’ module is confined by more walls than the ideal two-dimensional problem, this explanation could indicate a source of error. The errors of the experiments are not provided in the article.

It would also not be clear why the lower experimental concentrations for $C_{in} = 3$ kg·m$^{-3}$ from Figures 4.4c and 4.4d result in one case in a higher experimental flux compared to the simulations and in another case in a lower permeation. However, given the experimental uncertainties and the much lower errors for the permeate fluxes for this concentration, a simple question of measurement accuracy could be the reason.

4.1.4 Case IV

Geraldes et al. [2002] treated aqueous solutions of Na$_2$SO$_4$, sucrose and PEG1000 (polyethylene glycol 1000 g·mol$^{-1}$) with the flat-sheet nanofiltration membrane CDNF501 (SEPA-REM) installed in an asymmetric channel (that is, limited by one impermeable wall). The effective filtration zone measured 20.0 cm × 3.0 cm × 0.2 cm (lenght $L$ × width $w_l$ × channel full-height $d$) and possessed three independent collectors which collected the permeate generated up to a distance of 1.5 cm from the inlet (collector 1), between 1.5 cm and 3.0 cm (collector 2) and between 3.0 cm
and 6 cm (collector 3) measured from the entrance of the membrane module. Experimental results are provided for the three collectors only. For each substance, $C_{in} = 7\text{ g\cdot kg}^{-1}$ was tested at $T = 25^\circ\text{C}$ with three feed velocities $W_{in}$ (approximately 0.11 m\text{s}^{-1}, 0.23 m\text{s}^{-1} and 0.45 m\text{s}^{-1}) corresponding to $Re$ 250, 500 and 1000 for each one of the four values of pressure, 1, 2, 3 and 4 MPa. In our simulations, the physical properties $\rho_0$, $\mu_0$ and $D_0$ and the osmotic pressures are calculated with the expressions presented by the authors. The membrane water permeability is given as $I_0^{-1} = 1.4 \times 10^{-11} \text{ m\cdot Pa}^{-1}\cdot \text{s}^{-1}$.

The authors describe the transmembrane solute transfer by means of a model of
hindered transport inside the membrane pores, relating its coefficients to the local membrane surface concentration or intrinsic rejection ([Geraldes et al., 2002]).

For each solute, the model’s coefficients are concentration- and pressure-dependent and can be calculated from data provided by the authors. These data have been determined by the authors by fitting the model’s equation to experimental data – we presume to average apparent rejection rates – at high feed velocity (hence lower concentration polarization) corresponding to $Re = 1000$. By considering an averaged version of Equation 3.143 for writing the expression of intrinsic rejection, it is possible to estimate solution-diffusion permeability coefficients $B$ for the solutes at different pressures and concentrations. In our simulations, we adopted for each solute and $C_m = 7 \text{ g}\cdot\text{kg}^{-1}$ a unique permeability value averaged over the pressure values tested by the authors. This gives $B_{\text{Na}_2\text{SO}_4} = 9.5 \times 10^{-8} \text{ m}\cdot\text{s}^{-1}$, $B_{\text{sucrose}} = 3.7 \times 10^{-8} \text{ m}\cdot\text{s}^{-1}$ and $B_{\text{PEG}1000} = 2.2 \times 10^{-8} \text{ m}\cdot\text{s}^{-1}$.

Figure 4.5 contains the comparisons between the numerical predictions of permeate flux and all experimental values available.

The numerical predictions of permeate flux are very accurate for the $\text{Na}_2\text{SO}_4$ solution, with errors between $-3\%$ and $7.5\%$, and satisfactory for the sucrose solution, with errors below $20\%$. With the PEG1000 solution, they are in many cases above $30\%$, rising up to $72.5\%$ in the worst case. With both macromolecular solutes, the predictions are always overestimated when compared to the experiments; the errors are considerably lower for $P_m = 10 \times 10^5 \text{ Pa}$. Owing mainly to lower solute diffusion coefficients, the Schmidt numbers of the PEG1000 and sucrose solutions are considerably higher than for the $\text{Na}_2\text{SO}_4$ already in the feeds: 3021 and 1745 against 825. The simulations indicate a very important polarization for the macromolecular solutions. Indeed, for $P_m = 40 \times 10^5 \text{ Pa}$, the ratios of membrane surface concentration to feed concentration are near 43 and 36 for $Re$ of 250 and 1000 respectively with the PEG1000 solutions, and near 35 and 27 for $Re$ of 250 and 1000 respectively with the sucrose solutions. The corresponding surface Schmidt numbers in the end of the flow channel would achieve 17900 and 13130 with the PEG1000 and 5370 and 3860 with sucrose. As for the salt solution, the ratios of membrane surface concentration to feed concentration\footnote{These concentrations exceed the validity range of the osmotic pressure laws reported in the article.} are near 9.7 and 7.4 for $Re$ 250 and 1000 respectively, what results in Schmidt numbers of order 1140 and 1068. The much higher Schmidt numbers\footnote{The influence of higher viscosity is not totally negligible and contributes to increasing the} have the effect of intensifying concentra-
CHAPTER 4. Model Validation and Comparison to Experiments

(a) Na$_2$SO$_4$ solution, collector 1.  (b) Na$_2$SO$_4$ solution, collector 2.  (c) Na$_2$SO$_4$ solution, collector 3.

(d) Sucrose solution, collector 1.  (e) Sucrose solution, collector 2.  (f) Sucrose solution, collector 3.

(g) PEG1000 solution, collector 1.  (h) PEG1000 solution, collector 2.  (i) PEG1000 solution, collector 3.

Figure 4.5: Comparison between the experimental permeate fluxes from [Geraldes et al., 2002] collected in the first, second and third collectors for all substances, driving pressures and feed velocities and the numerical simulations.
tion polarization, thereby strongly reducing the permeate flux. Since the numerical model considers a constant, concentration-independent Schmidt number, it ignores such effects and overestimates the permeation.

The comparison of simulated and experimental apparent rejection rates for all $Re$ together shows that the simulations are frequently very satisfactory, and sometimes underestimating, specially in the last collector\(^3\).

- For the $\text{Na}_2\text{SO}_4$ solution: 0.986–0.993 (sim.) and 0.99–1 (exp.) in the collector 1, 0.970–0.987 (sim.) and 0.98–0.99 (exp.) in the collector 2, 0.953–0.982 (sim.) and 0.975–0.99 (exp.) in the collector 3;
- For the sucrose solution: 0.988–0.996 (sim.) and 0.99–1 (exp.) in the collector 1, 0.972–0.993 (sim.) and 0.99–1 (exp.) in the collector 2, 0.952–0.992 (sim.) and 0.985–0.995 (exp.) in the collector 3;
- For the PEG1000 solution: 0.990–0.997 (sim.) and 0.995–0.9975 (exp.) in the collector 1, 0.975–0.995 (sim.) and 0.99–0.9975 (exp.) in the collector 2, 0.956–0.995 (sim.) and 0.99–0.9975 (exp.) in the collector 3.

Knowing that the simulated permeate fluxes were most often higher than the experimental values, the concentration gradients simulated across the membrane would be expected to be lower than during the experiments and the rejection rates accordingly higher. This rationale being countered by the rejection values above, the solute permeability values used for the simulations seem to be overestimated.

### 4.2 Application to Spacer-Filled Flow Channels

A number of techniques exist for reducing the concentration polarization layer in pressure-driven applications in order to attenuate the deleterious consequences it causes\(^4\) and so maximize process performance. The use of rotating or vibrating membrane modules, of pulsatile flows, the sparging of gases into the flow channel or the use of “spacers” are a few examples [Ghidossi et al., 2006]. In the following, we focus on membrane modules whose feed channels are filled with spacers. The

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\(^3\) Simulated and experimental rejections become noticeably higher as $Re$ increases because of the reduction of the polarization layer, what increases the permeate flux and also reduces the solute transfer across the membrane.

\(^4\) Including considerations of energy consumption.
literature on the subject is vast and very detailed, what is out of the scope of this thesis, therefore only some topics are briefly cited.

After these introductory topics, we pursue the validation of our model for spacer-filled flow channels.

### 4.2.1 Overview

#### 4.2.1.1 Spacers

The so-called (feed) spacers are net-like arrangements of filaments (meshes, grids) placed in the feed channel of certain membrane modules. Some examples are presented in Figure 4.6. The diameter of the filaments, their number, the inter-filament distance and inter-filament angle are, in addition to the channel height and to the axial $Re$ number, key parameters which determine the effects of the spacers on the flow and concentration patterns. They are used to enhance mass transfer coefficients, enhancing the shear stress in the vicinity of the membrane and promoting some mixing, reducing by these means the polarization layer and retarding fouling, generating however higher pressure drops [Da Costa et al., 1991; Ghidossi et al., 2006; Schock and Miquel, 1987; Schwinge et al., 2004]. Flux enhancements of 3 to 5 times can be achieved [Da Costa et al., 1991]. The feed-side spacers also have the function of providing the flow channel (for the feed/retentate) between two membranes put face-to-face [Da Costa et al., 1991; Dow, d; Schwinge et al., 2004]. It should be noticed that, even if these structures are sometimes termed “turbulence promoters”, the $Re$ numbers are not high enough for reaching fully developed turbulence; the denomination “eddy promoters” would be more adequate [Ghidossi et al., 2006; Schwinge et al., 2004]. Spacers (fillers) can be used in permeate channels too.

![Figure 4.6: Examples of feed spacers. Figure from Da Costa et al. [1991].](image)
4.2.1.2 Spiral-Wound Modules

Spacers are used in some flat-sheet membrane modules and are the rule in the broadly used spiral-wound modules (SWM), the subject of a subsequent section of this Chapter.

In a SWM module, a large-size membrane leaf is composed of two membrane sheets glued back-to-back; in the zone between the sheets of a leaf, there exists a spacer which provides the channel for the permeate to flow. In three edges of the leaf, the sheets are glued together in narrow, delimited zones (glue lines). The non-glued side is connected to and sealed against a tube aimed at collecting the permeate from all leaves. In a SWM, from one to more than 30 leaves, separated by feed spacers, may be rolled around the permeate collector. The feed solution enters the module (installed in a pressure vessel) through the spacer-filled feed channels, flows along the membranes parallel to the permeate collector and exits them on the opposite side as retentate. The permeate flows spirally along the curved permeate channel to the permeate collector tube. Figure 4.7 illustrates different aspects related to a SWM. These modules are very popular in RO, NF and UF because of a good balance between packing density, permeation rate, fouling control and ease of operation, even though they are not free from traditional problems in the membrane field like concentration polarization and fouling [Dow, d; Schwinge et al., 2004].

![Exploded view of a spiral-wound membrane module.](image1)

![Frontal view of a spiral-wound membrane module.](image2)

Figure 4.7: Illustration of a spiral-wound membrane module. Figures from Baker [2004, p. 144].
4.2.2 Notions of Modeling of Spiral-Wound Modules

The spiral-wound module has a very complex geometry from the point of view of transport phenomena modeling. Modeling efforts\(^5\) are spent in analyzing both full-scale modules and more fundamental problematics straightly related to the presence of feed spacers; the latter case is usually carried out by integrating CFD analyses. The flow on the permeate side is frequently considered. In the field of spiral-wound module modeling, the attempts range from “the extremes of detailed description of transport phenomena at small scale” to the “macroscopic phenomenological-type simulation of the entire separation process in a module” [Kostoglou and Karabelas, 2009]! Figure 4.8 synthesizes well the purviews of these efforts:

<table>
<thead>
<tr>
<th>Modelling approach</th>
<th>SWM modelling</th>
<th>CFD modelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale</td>
<td>Analytical/numerical</td>
<td>Numerical</td>
</tr>
<tr>
<td></td>
<td>SWM model</td>
<td>Several spacer filaments in the flow channel</td>
</tr>
<tr>
<td>Interest</td>
<td>Flow patterns and flux distribution across the SWM leaf, SWM productivity</td>
<td>Fundamental understanding of local fluid flow (recirculation regions), mass transfer and shear stress patterns</td>
</tr>
<tr>
<td>Results</td>
<td>SWM design and optimisation</td>
<td>Spacer design and optimisation</td>
</tr>
</tbody>
</table>

Figure 4.8: Overview of modeling scopes for SWM. Figure from Schwing et al. [2004].

Two generic conclusions need to be highlighted:

- The pressure drop is enhanced in spacer-filled channels and reaches significant values (from 0.2 bar·m\(^{-1}\) up to 0.8 bar·m\(^{-1}\) excluding inlet and outlet pressure losses [Schock and Miquel, 1987]). Flows in these channels show a pressure loss comparable to transitional or fully turbulent flow [Da Costa et al., 1991; Schock and Miquel, 1987; Schwing et al., 2004];

- Large recirculation regions and eddy mixing exist near the filaments, where local velocities\(^6\) and shear rates are magnified. This reduces the boundary layer thickness and membrane wall concentration. The concentration polarization layer in a spacer-filled channel is different from that in an empty feed

\(^5\) The ratio of the membrane thickness to the radius of curvature of the flow channels being small, the curvature of the channels in spiral-wound geometry is *usually* neglected [Kostoglou and Karabelas, 2009; Nagy, 2012, p. 45; Schwing et al., 2004].

\(^6\) The overall velocity in the spacer-filled channel is higher than in an empty channel because of the reduction of the cross-section in the former [Schock and Miquel, 1987].
It is of interest to note that Sherwood correlations representative of laminar flow have been derived in the literature from the same applications for which the pressure drop was comparable to non-laminar flow [Da Costa et al., 1991; Schwinge et al., 2004]. Sherwood correlations typical of turbulent flow have however also been found [Da Costa et al., 1991; Schock and Miquel, 1987].

Since we are at it: an analytical solution using Berman’s perturbation technique has been derived in Chatterjee and Belfort [1986] for solving the Navier-Stokes equations for the flow of pure solvent in an annulus with two porous walls and without spacers, subject to uniform withdrawal and injection of fluid. The geometry represents an idealized spiral wound module.

4.2.3 Alternative Simulation Approach

The solute transfer in a spacer-filled feed channel is affected by two contrary and simultaneous effects: mixing promoted by the spacers and concentration polarization brought about by the permeate flux.

Acknowledging that the solute distribution in a cross-section of the feed channel is neither fully mixed nor fully polarized, Zhou et al. [2006] suggested that the salt concentration on the membrane surface would be locally function of a polarization factor $f_P$ describing the “degree” of concentration polarization in the channel. It was chosen so as to increase monotonically with the permeate flux $U(d, Z)$ (primary cause of concentration polarization) and be bounded between 0 (for complete mixing) and 1 (for undisturbed polarization). With our notations:

$$f_P = 1 - \exp \left[ -\frac{U(d, Z)d}{D_{HD}} \right]$$

The coefficient $D_{HD}$ was conceived as an indicator of the depolarization effect engendered by the spacers and was termed “hydraulic dispersion coefficient”. It has an analogy with the molecular diffusion coefficient $D_0$, to which it is equal in the absence of spacers, but can exceed it by orders of magnitude. Even if it is unbounded mathematically, $D_{HD}$ will reach on a case-by-case basis an upper boundary representing conditions of very high mixing or depolarization (approximately $D_{HD} \sim 8D_0$ in [Zhou et al., 2006]).
A key drawback of an approach utilizing the concept of hydraulic dispersion coefficient is its prediction. As far as we know, no method exists for this specific purpose, its determination relies on trial and error. Anyway, once known, $D_{HD}$ could be a simple way for carrying out simulations which take into account the effects of the feed spacer upon the process outputs.

We evaluate in the next sections the numerical results obtained with our numerical model using the concept of $D_{HD}$. Comparison to data from the literature and to our own experiments will be presented.

### 4.2.4 Case V

Zhou et al. [2006] treated aqueous solutions of NaCl of initial concentrations 0.5 g·kg$^{-1}$, 1.0 g·kg$^{-1}$ and 3.0 g·kg$^{-1}$ at $W_{in} = 0.075$ m·s$^{-1}$ and $T = 25^\circ$C up to $20 \times 10^5$ Pa with the membrane 2540SW (Koch Membrane Systems) in a long series array of spiral-wound modules (each 1.016 m long with a diameter of 6.35 cm). The modules were installed in two pressure vessels connected in series. A total of 4 modules was used, the effective filtration zone being given by the authors: 4 m long ($L$) and 1.2 mm high ($d=0.6$ mm, symmetric flow channel). The membrane water permeability is calculated from the membrane resistance value informed: $I_0^{-1} = 1.19 \times 10^{-11}$ m·Pa$^{-1}$·s$^{-1}$. No solute permeability coefficient is provided, but rejection is reported at 0.99. In our simulations, the physical properties $\rho_0$ and $\mu_0$ and the osmotic pressures are calculated with the expressions presented by Geraldes et al. [2002].

The authors employ $D_{HD} = 1.8 \times 10^{-8}$ m$^2$·s$^{-1}$, value about ten times higher than $D_0$. The replacement of $D_0$ by $D_{HD}$ is transposable to the Schmidt numbers. We shall speak of an effective (“apparent”) Schmidt number $Sc_{app}$ in this case [Lopes et al., 2014]. Here, $Sc_{app} \sim 50$ (for $Sc \sim 560 - 580$). We also simulate one case for a hydraulic dispersion coefficient $5D_{HD} = 9.0 \times 10^{-8}$ m$^2$·s$^{-1}$ equivalent to $Sc_{app} \sim 10$. Figure 4.9 presents the comparison between the experimental results and our numerical simulations.

The use of the molecular diffusion coefficient results in severe underestimation of the permeate flux, even more for higher concentration polarization, that is, higher pressures and concentrations (the order of magnitude of the errors lies between 30%-40% for the highest concentration, 20%-30% for the intermediate concentration and 10%-20% for the lowest concentration). The improvement of the
predictions when $D_{HD}$ is employed is evident. This value of dispersion coefficient reproduces a situation of very low polarization already, for $5D_{HD}$ does not yield any significant difference (illustrated only for $C_m = 3.0 \text{ g·kg}^{-1}$). The low polarization for a range of operating conditions is also indicated by the linear segments spanning to approximately $10 \times 10^5 \text{ Pa}$. That said, the agreement between experiments and predictions becomes worse (up to $-15\%$) starting from $11 \times 10^5 \text{ Pa}$ for the two lowest concentrations and from $13 \times 10^5 \text{ Pa}$ for the highest concentration, even though the form of the plots correspond to those of the experiments. Since $Sc_{app} \sim 50$ (or $Sc_{app} \sim 10$) represents a very depolarized state, the concept behind $D_{HD}$ suggests that the recourse to this coefficient could not be “enough” for reproducing all conditions of (de)polarization in spacer-filled channels.

In spite of these considerations, it should be noticed that the 4 m-long module used in this experiments is, as reported by the author, composed of 4 equal modules connected in series. Spiral-wound modules are connected to each other in such a way that the permeate which exits one module flows, before it enters in the coming module, through an empty volume where the connections between the neighboring modules is done. That is, the flow is not continuous and, particularly, the polarization layer is disturbed at the connections (3 in this case). Our model does not capture these effects of course, it describes an increasing, continuous polarization layer and, in this case the simulations are expectedly underestimated. This could explain the worse agreements at higher polarization conditions in Figure 4.9.
4.2.5 Our Experiments in Spiral-Wound Geometry

Given the difficulties for comparing our simulations to results from the literature (unknown input parameters, parameters determined based on radical assumptions—e.g. like neglecting the polarization layer—etc.), we needed to perform our own experiments.

We carry on comparing our numerical predictions with experimental results for the spiral-wound geometry. From this point on, our own experiments provide basis for further discussions.

4.2.5.1 Materials and Methods

4.2.5.1.1 Pilot Module and Experiments

We carried out experiments with the pilot test module (PIGNAT OSM/2000, France) for spiral-wound membranes situated in the Chemical Engineering pilot hall of École Centrale de Marseille at the university campus of Saint-Jérôme in Marseille.

The pressure vessel of the test module accommodated one commercial spiral-wound module 1.016 m long with a diameter of 9.9 cm. A feed tank of 100 L was filled with the desired volume of municipal water; this water was previously filtered in a cartridge filter for the removal of suspended particles (polyester filtering net: ATLAS FILTRI RL SX 50 micron, Italy; housing: ATLAS FILTRI Plus 2P SX, Italy). A cooling coil fed with municipal water was installed in the tank for controlling its temperature (manually). The liquid was pumped by a vertical multistage electric centrifugal pump (EBARA EVM3 26F5, Italy). Part of it was by-passed, controlled by means of a diaphragm valve and returned to the feed tank; the rest was fed into the membrane module (details further on the text) after passing through the feed valve (ball-type). The latter was installed vertically, so that all streams flowed downwards. Once they had left the membrane module, the retentate and the permeate flowed upwards through rotameters (retentate: KOBOLD KSA 35 4030 H K50, Germany; permeate: KOBOLD KSA 35 4006 H K32, Germany) back to the feed tank. The by-pass valve and a needle valve on the retentate outlet allowed to control the inlet pressure and the feed flow. The former was measured by
pressure gauges on the feed line and right after the retentate outlet. A flow layout in closed loop was used (all streams were recycled to the feed tank). The parts in contact with the liquid were all made of stainless steel, except for the copper cooling coil, the vinyl tubings and the plastic rotameters and feed tank.

The experiments were carried out either with pure water or with salt solutions. Solutions of different reagent-grade salts and concentrations were prepared and added to a previous volume of water (∼ 60 L) in the tank: Na₂SO₄ (Alfa Aesar, Germany), MgSO₄·7H₂O (Sigma-Aldrich, France) and NaCl (Sigma-Aldrich, France). The conductivity and temperature of the feed (tank), retentate and permeate were measured with a conductivity meter (Eutech/Oakton CON 11, Singapore/United States of America) equipped with a conductivity electrode with built-in temperature sensor (EC-CONSEN91W 35608-50). Calibration lines converted conductivities to concentrations. A photo of the pilote module is shown in Figure 4.10.

Figure 4.10: Pilot test plant for spiral-wound modules used for our experiments.

A preparation phase preceded each experiment. Immediately after the start-up, a waiting time of approximately 2 min with the feed valve closed was respected. An experiment with a salt solution started by first running the system with water at lowest pressure for 10 min with the by-pass and permeate valve completely
opened, the feed valve being gradually but completely opened in order to avoid severe pressure or flow changes in the membrane module. The system would then be shut down: the feed valve closed first (and relatively slowly), and only then the by-pass and permeate valves, so that the membrane could be kept in water at low pressure\textsuperscript{7}. The remaining water volume would be discarded, the feed tank refilled with new water, an amount of salt solution added to it and the system restarted. It ran for 3 min under these conditions in order to homogenize its content with the dead volumes present in the system. Afterwards, the feed valve was opened progressively but completely and let ran for 3 min.

Followed the setting of the first combination of inlet pressure (the lowest of all tested values) and feed flow rate by controlling the by-pass and retentate valves. After 30 min, the permeate flux and concentration would be measured a first time and from then on remeasured each 5 minutes until no changes were detectable and steady-state operation ensured. Particular attention was paid to the permeate concentration: it took much longer to stabilize than the permeate flux. At highest concentration values, the permeate concentration of the first operating condition\textsuperscript{8} (low pressure) would constantly drop during approximately 1.5 h before reaching a stable value. The subsequent operating conditions needed shorter periods. The temperature of the solution in the feed tank was monitored regularly and the flow rate of the cooling coil adjusted in order to keep the content of the tank at $25 \pm 1 \degree C$. The maximum inlet pressure reached by the system was about 22 bar (upper limit of $P_{in}$ in our experiments).

When steady state was reached, all measurements were undertaken. The conductivity and the temperature of samples of the feed, of the permeate and of the retentate were measured. Because of the flow layout which recycled all the streams, the feed concentration did not vary. The permeate and retentate flow rates were read on the flow meters or, in the case of too low retentate flow rates, by timing how long it took to fill a 2 L-graduated cylinder\textsuperscript{9}. All the volumes withdrawn for the measurements were recycled to the feed tank. Once the measurements were performed, the next combination of inlet pressure and feed velocity was set and the protocol reapplied. Various values of $C_{in}$, $P_{in}$ and $W_{in}$ were tested. Notice that city water had a conductivity of $\sim 400 \mu S \cdot cm^{-1}$ and the conductivity of the perme-

\textsuperscript{7} Systematic procedure whenever the module was shut down.
\textsuperscript{8} Presumably the closest one to a mainly diffusive regime from the point of view of the transmembrane salt transfer.
\textsuperscript{9} In this case, the measurements were done at the outlet of the tubings shown discharging in the feed tank in Figure 4.10.
ate obtained with the RO membrane of about 2 µS·cm⁻¹ (practically not differing from that measured with distilled water, typically below 1 µS·cm⁻¹), thereby not disturbing the permeate conductivity and confirming that it was not necessary to perform the experiments with distilled water. At the end of the experiments with salt solutions, the membrane would be rinsed for tens of minutes with city water above the maximum pressure used during the experiments until the feed conductivity dropped to the city water conductivity and the permeate conductivity to approximately 2 µS·cm⁻¹.

Experiments with pure water aimed at determining the membrane water permeability followed a similar protocol except for the addition of solute. They were performed before each cycle of tests with salt solutions. Steady state would be reached within 5 min-10 min for the first operating condition and in less than 5 min for the subsequent conditions. Measurements were undertaken during increasing- and decreasing-pressure cycles.

The experiments took place over several days in different periods of a year. The membrane was kept immersed in municipal water in the interim, and the system ran for some minutes from time to time. Measurements of water permeability performed with the RO membrane indicated no detectable modification of $I^{-1}_0$ within consecutive weeks, and an enhancement of only 4% in a period of one year.

### 4.2.5.1.2 Membrane Module

The polyamide thin-film composite reverse osmosis spiral-wound membrane module BW30-4040 (Dow Filmtec, United States of America) was employed [Dow, a]. It is composed of the same membrane sheets as those used in section 2.2.2, membrane BW30, recommended for brackish water applications and achieving high salt rejection.

The module has a nominal length of 1.016 m and a diameter of 9.9 cm. As for the channel height, the feed spacer is informed by the manufacturer to be 34 mil high\(^\text{10}\), that is, $d = 0.4318$ mm. We could not perform a module autopsy but measured the length occupied by end-caps and connectors, length which exceeds those presented in the product data sheet; the membrane length is thereby set to $L = 0.94$ m. Considering square membrane leaves, the width of each sheet will be $w_l = 0.94$ m. The module has a nominal filtration area of 7.6 m². It must be

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\(^{10}\) “mil” denotes a thousand of inch (0.0254 mm).
composed of an integer number of membrane sheets, from what we conclude that $L$ and $w_l$ must be overestimated because they result in more than 8 and less than 9 sheets. Since a membrane leaf is made up of two membrane sheets, we keep a total of 8 membrane sheets (4 membrane leaves), i.e. 5 feed flow channels\textsuperscript{11}, consequently 3 symmetric and 2 asymmetric (the latter face the outer wrap of the module).

### 4.2.5.2 Results and Discussions

#### 4.2.5.2.1 Reverse Osmosis

Experimental and simulation results are most of the time presented together for conciseness.

The membrane water permeability was determined from the slopes of plots of permeate flux vs. transmembrane pressure and are indicated when the results are presented. Their determination was carried out using points in increasing- and decreasing-pressure cycles and showed that hysteresis did not occur (due to compaction or other effects like in Chapter 2). The most suitable value of $Sc_{app}$ is an unknown and was fitted. Solute permeability coefficients ($B$) are also not known a priori and were fitted to the experimental results. In our simulations, the physical properties $\rho_0$, $\mu_0$ and $D_0$ were calculated with the expressions in Geraldes et al. [2002] and the osmotic pressure with van’t Hoff’s law. Figure 4.11 shows the permeate fluxes and rejection rates obtained experimentally and numerically with a solution of $NaCl$ of $C_{in} = 5.3 \text{ g} \cdot \text{L}^{-1}$ up to $P_{in} = 20 \times 10^5 \text{ Pa}$ with\textsuperscript{13} $Re = 105$ ($W_m = 0.055 \text{ m} \cdot \text{s}^{-1}$) and $I_0^{-1} = 6.84 \times 10^{-12} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$. Different values of $Sc_{app}$ (c.f. section 4.2.4) starting from 120 are simulated in addition to the limiting, molecular Schmidt number $Sc = 600$. The solute permeabilities tested were $B = 10^{-8} \text{ m} \cdot \text{s}^{-1}$ and $B = 10^{-7} \text{ m} \cdot \text{s}^{-1}$.

If the entire range of $P_{in}$ is to be considered, $Sc_{app} \sim 200$ or $Sc_{app} \sim 150$ could be seen as “best” fitting value of the permeate flux $U_{av}$. The distinction of the most adequate $Sc_{app}$ value is however not evident. For low-intermediate $P_{in}$, $Sc_{app} \sim 200$ and $Sc_{app} \sim 300$ are appropriate for $U_{av}$. For very low pressures, i.e. low polarization and eddy mixing conditions, we approach $Sc = 600$; for highest pressures,

\textsuperscript{11} The knowledge of the number of flow channels is necessary for calculating the feed velocities in the feed channels.

\textsuperscript{12} For $L = w_l = 0.96 \text{ m}$.

\textsuperscript{13} $Re$ calculated from the definition of hydraulic diameter.
$Sc_{app} \sim 150$ starts to become a potential choice. The effect of the Schmidt number is also seen in the plot of $R_{av}$ vs. $U_{av}$ because not all values of Schmidt are capable of yielding appropriate values of rejection rate and permeate flux simultaneously, so that both variables must be evaluated concurrently. Judging by this plot, a $Sc_{app}$ around 150 $\sim$ 200 seems more adequate. Notice that the depolarization effect becomes proportionally less sensible to the decrease of Schmidt value for $Sc_{app} < 200$ as mentioned in section 4.2.3. The solute permeability value has practically no effect on $U_{av}$ but is crucial for the solute rejection (but the effect on $U_{av}$ was perceptible and was in agreement with the simulations from Chapter 3). $B = 10^{-8}$ m·s$^{-1}$ and $B = 10^{-7}$ m·s$^{-1}$ are clearly limit values for $R_{av}$. For the former value, all plots are overlapped because the rejection rate is too high.

Figure 4.12 shows the permeate fluxes and rejection rates obtained experimentally with pure water and aqueous solutions of sodium chloride of different initial con-
centrations (up to the previous one) under the same conditions as before and the numerical predictions for $B = 10^{-7}$ m·s$^{-1}$ and $Sc_{app} = (1/4)Sc$. Good agreement is verified for the permeate fluxes for all pressures and for the rejection rate at higher pressures.

![Graph showing Rv vs Uav for different concentrations](image)

![Graph showing Uav vs Pm for different concentrations](image)

Figure 4.12: Experimental results with pure water and aqueous solutions of NaCl of different $C_{in}$ and $Re = 105$ ($W_{in} = 0.055$ m·s$^{-1}$) and the corresponding numerical simulations performed considering $Sc_{app} = (1/4)Sc$ and $B = 10^{-7}$ m·s$^{-1}$. Adapted from Lopes et al. [2014].

We sum up the observations based on these experimental results [Lopes et al., 2014]:

- The use of an effective Schmidt number $Sc_{app}$ about 3 or 4 times lower than the molecular $Sc$ made possible a satisfactory reproduction by simulation of the experimental results of permeate flux and rejection rate in most of the range of operating conditions. Not all values of $Sc_{app}$ fit both permeate flux and rejection rate, so that the determination should include the analysis of both.
• The influence of the solute permeability value was negligible on the permeate flux but significant when analyzing the rejection rate. This consideration was more deeply discussed throughout section 3.2.5.1 in Chapter 3;

• \( B = 10^{-8} \text{m} \cdot \text{s}^{-1} \) and \( B = 10^{-7} \text{m} \cdot \text{s}^{-1} \) were suitable boundaries for the solute permeability coefficient.

The uncertainties about \( Sc_{\text{app}} \) and \( B \) are a limitation for the application of our model as a predictive tool when dealing with spacer-filled modules. Nevertheless, we see that, once the permeate flux is fitted, what is essentially a matter of finding the appropriate \( Sc_{\text{app}} \), we can concentrate on the rejection rate which will be in this case a question of evaluating \( B \). Our discussions hereinafter are in large part organized in light of this “decoupled” analysis and focus on the determination of \( B \) and its behavior.

We show now some more results obtained with aqueous solutions of NaCl of initial concentration \( 1.4 \text{ g} \cdot \text{L}^{-1} \), \( 5.2 \text{ g} \cdot \text{L}^{-1} \) and \( 10.0 \text{ g} \cdot \text{L}^{-1} \) and\(^{14} \) \( Re \sim 210 \left( \frac{W_i}{100} \right) \) up to \( P_m = 20.5 \times 10^5 \text{ Pa} \) for \( I_0^{-1} = 7.13 \times 10^{-12} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1} \). Different values of \( Sc_{\text{app}} \) and solute permeability are simulated\(^{15} \). The latter are expressed in the graphs in the form of the ratio \( B/(I_0^{-1}iRT) \) (mol·m\(^{-3} \)) as in Equation 2.49 in Chapter 2. Figures 4.13, 4.14 and 4.15 show the results of permeate flux and rejection rate. The definition of the Péctel numbers seen in the plots is not altered compared to their previous definitions; they keep being calculated with \( D_0 \) and not with \( D_{HD} \).

Again, \( Sc_{\text{app}} < 150 \) is adequate for the simulations and the solute permeability has a negligible effect on the permeate flux or averaged permeation Péctel (\( P_{eav} \)). We focus on the rejection rates and solute permeability values. We remark that the most suitable fitting value of \( B/(I_0^{-1}iRT) \) decreases as \( C_{in} \) is increased, little but recognizably: \( B/(I_0^{-1}iRT) \sim 1 \text{ mol} \cdot \text{m}^{-3} \) for \( C_{in} = 1.4 \text{ g} \cdot \text{L}^{-1} \), \( B/(I_0^{-1}iRT) \) exceeds 1 mol·m\(^{-3} \) by little for \( C_{in} = 5.2 \text{ g} \cdot \text{L}^{-1} \) and \( B/(I_0^{-1}iRT) \sim 2.5 \text{ mol} \cdot \text{m}^{-3} \) for \( C_{in} = 10.0 \text{ g} \cdot \text{L}^{-1} \). The rejection rate shows to be very sensitive to the membrane permeability which is, in turn, sensitive to concentration. In usual dimensions, for \( I_0^{-1} = 7.13 \times 10^{-12} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1} \), the approximate solute permeability coefficients deduced from the previous ratios \( B/(I_0^{-1}iRT) \) are presented in Table 4.4. They have the same order of magnitude, \( 10^{-8} \text{ m} \cdot \text{s}^{-1} \), and increase with concentration.

We could in principle expect the best-fitting \( B \) to vary according to \( P_m \), that

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\(^{14} \) Re calculated from the definition of hydraulic diameter.

\(^{15} \) For \( L = w_l = 0.94 \text{ m} \).
is, according to the extent of concentration polarization (i.e. to the membrane surface concentration) to some noticeable extent. However, the inspection of the rejection plots reveals that, for each $C_{in}$, a unique value of $B/(I_0^{-1}iRT)$ fits well the points in the entire range of $P_{in}$. For modifications to be perceptible, we speculate that the membrane surface concentration would need to vary as a result of $P_{in}$ of roughly the same proportion as the feed concentrations or at least that their order
CHAPTER 4. Model Validation and Comparison to Experiments

Figure 4.14: Experimental results with an aqueous solution of NaCl of $C_{in} = 5.2 \text{ g} \cdot \text{L}^{-1}$ ($P_{e_{in}}^{osm} = 0.91$) and $Re = 212$ ($W_{in} = 0.11 \text{ m} \cdot \text{s}^{-1}$) and the corresponding numerical simulations performed for different Schmidt numbers and values of $B/(I_0^{-1}iRT)$ (mol·m$^{-3}$).

of magnitude would need to change considerably. Table 4.5 gives the averaged membrane surface concentrations$^{16}$, $C_{av}^M$, for different conditions. It shows that the modification of the membrane surface concentration for a same $C_{in}$ and very different $P_{in}$ occurs within rather narrow ranges which do not overlap with those of other $C_{in}$. Of course, since the dependences of $B/(I_0^{-1}iRT)$ on concentration and on pressure are unknown, the discussion remains qualitative but substantiates the fact that a unique value of $B$ is adequate for each $C_{in}$ in the range of tested values.

The ideal experimental situation for the determination of $B$ by such analyses is that of no concentration polarization or complete mixing so that the concentration gradient across the membrane would be exactly known. The depolarization induced by the spacers contribute to this to some extent. However, this effect is not described by our model. On the other hand, the spacers cannot neutralize the

$^{16}$ $C_{av}^M = c^M_{av}C_{in}$ where the calculation of $c^M_{av}$ is showed in Equation 4.2.
concentration of the retentate consequent to the permeation of solvent, an effect captured by our model. The idea of the hydraulic dispersion coefficient or apparent Schmidt number is a sort of bridge between the effects. We are aware that it is not representative of the real physics of the problem and that it limits the use of the model to empiric, non-predictive approaches.

4.2.5.2.2 First Results in Nanofiltration

This subsection provides brief insights concerning experiments in nanofiltration and the corresponding numerical predictions with our numerical code considering solution-diffusion boundary conditions.

Tests were performed with the polyamide thin-film composite loose-nanofiltration spiral-wound membrane module NF270-4040 (Dow Filmtec, United States of America) [Dow, c]. It is composed of the same membrane sheets as those used in section
Table 4.5: Evolution of the averaged membrane surface concentration for different operating conditions. $Re \sim 210$.

2.2.2, membrane NF270, recommended for surface and groundwater applications and achieving low salt rejection but high rejection of organic compounds. The module has a 28 mil high feed spacer, that is, $d = 0.3556$ mm. The other data are the same as those seen with the RO membrane (including $L = w_f = 0.94$ m).

The membrane water permeability, $I_0^{-1} = 3.46 \times 10^{-11}$ m·Pa$^{-1}$·s$^{-1}$, was determined from the slopes of a plot of permeate flux vs. transmembrane pressure up to $P_m = 6.7 \times 10^5$ Pa$^{17}$. Figures 4.16 and 4.17 show the permeate fluxes and rejection rates obtained experimentally and numerically with solutions of Na$_2$SO$_4$ (up to $P_m = 11.4 \times 10^5$ Pa) and MgSO$_4$ (up to $P_m = 8.8 \times 10^5$ Pa). Different values of $Sc_{app}$ are simulated. Solute permeability coefficients and $Sc_{app}$ are not known a priori. In our simulations, the physical properties $\rho_0$, $\mu_0$ and $D_0$ were calculated with the expressions in Ahmad and Lau [2007] and the osmotic pressure with van’t Hoff’s law.

A first aspect is that $Sc_{app} \sim 150$ is a suitable value of Schmidt number for $U_{av}$ and $R_{av}$ (similarly to the cases with the RO membrane). We focus again on $R_{av}$. The rejections are relatively high (between 0.92 and 0.98) and can be fitted with a solute permeability coefficient. More precisely, $B/(I_0^{-1}iRT) \sim 1$ (or $B \sim 1.7 \times 10^{-7}$ m·s$^{-1}$) with MgSO$_4$ while Na$_2$SO$_4$ suggests a slightly lower permeability ratio, i.e. higher $B$. Sodium and magnesium sulfates are solutes of higher molar mass, so that a solution-diffusion mechanism may be expected to play a significant role in their permeation through the membrane. Under these conditions, our model is able to reproduce the trends of $U_{av}$ and $R_{av}$. It is however likely that the solute passages we found are explained to same extent by convection

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$^{17}$ The membrane was previously conditioned with pure water up to $P_m = 20 \times 10^5$ Pa.
and other effects. In such cases, our simulations of $R_{av}$ would induce verisimilar but not rigorous interpretations.

### 4.3 Analysis of the Permeability Values

In Chapter 2 (Table 2.4), we determined membrane salt and water permeabilities by carrying out osmotic-diffusive experiments with the RO membrane BW30. We will revisit these results and compare them to the ones fitted in this Chapter from experiments with the RO spiral-wound module. Indeed, the spiral-wound module contained the same membrane specification as the osmotic-diffusive experiments.

The three methods employed in this section for determining/comparing solute permeability coefficients were:
Figure 4.17: Experimental results with an aqueous solution of MgSO$_4$ of $C_{in} = 2.8\ \text{g}\cdot\text{L}^{-1}$ ($P_{e_{in}}^{osm} = 2.23$) and $Re = 235$ ($W_{in} = 0.15\ \text{m}\cdot\text{s}^{-1}$) up to $P_{n} = 8.8 \times 10^5\ \text{Pa}$ and the corresponding numerical simulations performed for different Schmidt numbers and values of $B/(I_0^{-1}\cdot RT)$ (mol·m$^{-3}$).

- Fitting the apparent rejection values obtained experimentally with the spiral-wound module (Fitting of $R_{av}$);
- For comparison, taking the values obtained in Chapter 2 (Table 2.4) by means of purely osmotic-diffusive experiments with a flat-sheet sample (Osm.-diff.);
- Determining $B$ by a “mixed method”, by multiplying the ratio between water and salt permeabilities determined in Chapter 2 via pure osmosis-diffusion (“$B/(I_0^{-1})$”) by the pressure-driven solvent permeability obtained experimentally with the spiral-wound membrane.

Table 4.6 summarizes the solute permeability coefficients determined by three methods:
<table>
<thead>
<tr>
<th></th>
<th>Fitting of $R_{av}$</th>
<th>Osm.-diff.</th>
<th>Mixed method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{in}$</td>
<td>$C^+_0$</td>
<td>$B$</td>
<td>$B$</td>
</tr>
<tr>
<td>(g·L$^{-1}$)</td>
<td>(g·L$^{-1}$)</td>
<td>(m·s$^{-1}$)</td>
<td>(m·s$^{-1}$)</td>
</tr>
<tr>
<td>$C^+_M$</td>
<td>$B$</td>
<td>$B$</td>
<td>$B$</td>
</tr>
<tr>
<td>(g·L$^{-1}$)</td>
<td>(m·s$^{-1}$)</td>
<td>(m·s$^{-1}$)</td>
<td>(m·s$^{-1}$)</td>
</tr>
<tr>
<td>1.4</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\leq$ 2.4</td>
<td>$5.6 \times 10^{-8}$</td>
<td>$-9.0 \times 10^{-8}$</td>
<td>$6.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>5.2</td>
<td>$\leq$ 7.7</td>
<td>$3.5 \times 10^{-8}$</td>
<td>$-$</td>
</tr>
<tr>
<td>10.0</td>
<td>$\leq$ 13.0</td>
<td>$8.8 \times 10^{-8}$</td>
<td>$-$</td>
</tr>
<tr>
<td>$-</td>
<td>$10.0</td>
<td>$3.6 \times 10^{-8}$</td>
<td>$10.0$</td>
</tr>
<tr>
<td>$-</td>
<td>$35.0</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$1.9 \times 10^{-7}$</td>
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<tr>
<td>$-</td>
<td>$35.0</td>
<td>$1.6 \times 10^{-7}$</td>
<td>$1.9 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 4.6: Values of sodium chloride permeability and related concentrations:
- estimated by fitting the apparent rejection values obtained experimentally with the spiral-wound module (Fitting of $R_{av}$);
- obtained in Table 2.4 (Chapter 2) by means of purely osmotic-diffusive experiments with a flat-sheet sample (Osm.-diff.);
- by a “mixed method”, multiplying the ratio between water and salt permeabilities determined in Table (Chapter 2) via pure osmosis-diffusion ("$B/(I_0^{-1})$") with a flat-sheet sample by the water permeability determined for the spiral-wound membrane.

The values for $C^+_0 = 35.0$ g·L$^{-1}$ were listed just for reference.
For similar concentrations (represented in a same line in Table 4.6), the differences between the values of $B$ found by fitting and determined by osmosis-diffusion (in Chapter 2) are not completely different in absolute value from the differences between the values of $B$ estimated by fitting and determined via the “mixed method” \(^{18}\). In the latter case, both values tend to increase with concentration. The order of magnitude of the coefficients determined by all methods is in most of the cases $10^{-8}$ m·s\(^{-1}\) or deviate little from it, but the absolute values are considerably different. These differences are high enough so as to affect the predicted rejection rates markedly.

The determination of $B$ for a pressure-driven application by means of a mixed osmotic-diffusive/pressure-driven method, that is, by multiplying the ratio between water and salt permeabilities determined via pure osmosis-diffusion by the water permeability determined both under pressure, would imply that the ratio $B/(I_0^{-1}iRT)$ is conserved by the membrane under osmosis-diffusion or under pressure, and even though the individual permeabilities might change\(^{19}\). This would be a “strong” hypothesis. Our results in Table 4.7 point out that the ratio is not conserved when the physical “boundary conditions” across the membrane are changed (pressure-driven or osmotic-diffusive mode). As shown in the Table, $B/(I_0^{-1}iRT)$ is lower when $B$ and $I_0^{-1}$ are both determined under pressure (columns “Fitting of $R_{av}$”) than when the ratio is determined directly during osmosis-diffusion (columns “Fitting of $R_{av}$”). As already mentioned, these differences are high enough so as to affect the predicted rejection rates markedly.

As for the values of salt permeability determined during pure osmosis-diffusion in Chapter 2, it is seen that they are not good estimations either for $B$ when the membrane operates under pressure.

At this point, some remarks should be made:

- Even though the spiral-wound membrane of this Chapter and the flat-sheet membrane sample of Chapter 2 have the same specification, they are not the same membrane. Also, the former is months older than the latter and has been always operated with municipal water while the flat-sheet with distilled

\(^{18}\) The latter method gives a slightly better agreement, but this should not be understood as a general tendency.

\(^{19}\) Our results in Table 2.4 (Chap. 2) pointed out that $I_0^{-1}$ can be one or two orders of magnitude lower in osmosis-diffusion than in pressure-driven mode. A difference of “ten times” has already been pointed out in the old literature [Goosens and Van Haute, 1978] with cellulose acetate membranes reinforced by the addition of mineral fillers (thus, very different from the membranes we tested).
CHAPTER 4. Model Validation and Comparison to Experiments

<table>
<thead>
<tr>
<th></th>
<th>Fitting of $R_{av}$</th>
<th>Mixed method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{in}$</td>
<td>$C_{M}^{av}$</td>
<td>$C_{0}^{+}$</td>
</tr>
<tr>
<td>(g·L$^{-1}$)</td>
<td>(g·L$^{-1}$)</td>
<td>(g·L$^{-1}$)</td>
</tr>
<tr>
<td>$B/(I_{0}^{-1}iRT)$</td>
<td>(mol·m$^{-3}$)</td>
<td>(mol·m$^{-3}$)</td>
</tr>
<tr>
<td>1.4</td>
<td>$\leq$ 2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>$\leq$ 5.2</td>
<td>$7.7$</td>
<td>1.8</td>
</tr>
<tr>
<td>10.0</td>
<td>$\leq$ 13.0</td>
<td>2.5</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 4.7: Ratios of salt to water permeability for different concentrations obtained by two methods. $B$ and $I_{0}^{-1}$ in the first method are both estimated under pressure with the spiral-wound membrane. The values of the second method are those from Table 2.3 (Chapter 2) where the ratio is determined directly from osmotic-diffusive experiments.

...water. Membrane aging and operation are known to modify the membrane properties as long times elapse;

- Due to material restrictions (pump), the spiral-wound membrane has never been subject to pressures above $\sim 22 \times 10^5$ Pa, while the flat-sheet sample has been conditioned up to $\sim 25 \times 10^5$ Pa. We have discussed in Chapter 2 that the maximal operating/conditioning pressure might have an influence on the membrane solvent permeability, and that solvent and solute permeability are not totally uncorrelated properties;

- The temperature of the system during the osmotic-diffusive experiments varied with the ambient temperature; with the SWM, it was constant (within $25^\circ$C $\pm 1$ $^\circ$C);

- Compared to a situation where no feed spacer is present, the membrane is known to be deformed mechanically under pressure by the spacer with a consequent increase in the values of $I_{0}^{-1}$ and $B$; tensile stresses in the deformed, stretched membrane caused by rearrangements of the polymeric chains would explain the modification of the permeability properties [She et al., 2013]. The existence of internal stresses when the membrane is subject to pressure has been suggested by some authors as reviewed in section 2.1.2.4.1 of Chapter 2.

In light of these considerations and possibly of others that we overlook, obtaining a precise value of solute permeability applicable to pressure-driven operation from values determined experimentally in osmotic-diffusive operation is not likely, at least not if mid to high pressures are considered. The membrane does not seem to
behave equally in both contexts. Nevertheless, the order of magnitude of the solute permeability in the former operating mode was coherent in our study with the values of solute permeability extracted from purely osmotic-diffusive experiments. This has its practical value. In our experiments with the spiral-wound membrane, rejections would be predicted above $\sim 0.9$ or more (roughly). $B$ proves to be a property sensitive to many factors deserving each very careful study and whose experimental control was often out of our reach.

The values of $I_\text{o}^{-1}$ determined experimentally with the RO and NF spiral-wound membranes are similar to those found during the pressure-driven conditioning of the flat-sheet samples in Chapter 2. As already mentioned, the “osmotic permeabilities” are lower than the “pressure-driven” water permeabilities by one or two orders of magnitude, what suggests that the transport mechanism induced by $\Delta P$ or by $\Delta \pi$ separately are not the same.

\section*{4.4 Chapter Conclusion}

The validation of our numerical model by comparing its predictions to experimental results yielded good results in general. It confirmed that the predictions of the permeate flux and of the rejection rate can be performed separately as long as reasonable parameters are used.

The rejection rate is particularly sensitive to the solute permeability coefficient. It was predicted satisfactorily whenever the transport parameters provided by the experimentalist were determined from values of membrane surface concentration, what represents an encouraging milestone. Simulations of rejection rate performed with salt permeability coefficients determined from bulk concentrations resulted in bad agreement between experience and simulation unless for low concentration polarization conditions. The findings highlight that the determination of transport parameters is of greatest importance for process performance prediction and shall integrate a thorough assessment of concentration polarization.

The validation of permeate fluxes showed to be more dependent on the overall conditions characterizing the cross-flow. They were good whenever the hypothesis of our model were satisfied by the experimental setup. Edge effects were alluded to as having an adverse effect for the comparison of simulation results to experiments. Indeed, their effects are out of the range of validity of our model which supposes
two-dimensional, fully developed cross-flow from the channel entrance up to its exit. For this reason, carrying out validations with long modules would be the optimum. The comparisons to experimental results evidenced that the neglect of the spatial variation of the physical properties of the solution, specially of the solute diffusion coefficient in the bulk, is appropriate in desalination applications. However, as soon as compounds producing high Schmidt numbers are to be treated and concentration polarization is a concern, the simplification is detrimental to process prediction. In addition to these points, we stress a general remark on the influence of the osmotic pressure law employed for the simulations. Van’t Hoff’s law and many phenomenological expressions are not adequate for calculating osmotic pressures in highly concentrated media, such as those corresponding to the membrane surface concentration subject to high polarization. This can lead to inaccuracies which can go unseen. Our numerical model is flexible in this regard, the osmotic pressure used by it can be easily adapted if available.

Spacer-filled channels are a standard situation in real-life applications and specially in spiral-wound modules. Our and other models do not describe the whole modifications engendered by the spacers in the flow channel (pressure drop included) but they can account to some extent for the (spatially varying) concentration of the feed/retentate as solvent permeates, provided that the evolution of the membrane surface concentration can be simulated somehow. The approach based on the replacement of the molecular solute diffusion coefficient or Schmidt number by a hydraulic dispersion coefficient or apparent Schmidt number which simulates an enhanced retro-diffusion of solute from the membrane surface toward the bulk showed to be capable of reproducing this evolution in many cases. The numerical model ceases to be a general predictive tool, but can still be envisioned as such if adequate ranges of apparent Schmidt number are found\textsuperscript{20}. Alternatively, the combination of our modeling approach with fine models focused on the description of the momentum and mass transfers in the flow channel would be a promising outlook. As a matter of fact, our model was able to reproduce the permeate fluxes and rejection rates with in RO and NF of different salts when the solute transport mechanism could be described by a mechanism predominantly of solution-diffusion type.

A major aim of the experiments carried out in this Chapter was to validate in pressure-driven operation the utilization of the solute permeability coefficients de-

\textsuperscript{20} What is a dully task.
termined for the RO membrane in Chapter 2 via osmotic-diffusive methods. It turned out that the salt permeability coefficients characteristic of pressure-driven operation were different from the osmotic-diffusive ones, what suggests that the membrane is sensitive to the hydrodynamic pressure to a degree capable of modifying its transport properties. Like in osmosis-diffusion, they were concentration-dependent. The orders of magnitude of both coefficients were however similar; the rejection rates predicted with the osmotic-diffusive salt permeabilities would not descend much below 0.9 instead of approaching unity. Fine process prediction requires however more accurate parameters.
Conclusions and Perspectives

The course of a separation by reverse osmosis and by other membrane processes is deeply dependent on the properties of the mixture to be treated, on the transport across the membrane and on the hydrodynamic conditions, concentration polarization and pressure drop in the flow channel. These parameters are correlated intimately at different extents. Therefore, the prediction of the performance of a membrane process in terms of permeate flux, rejection rate and retentate flow rate and concentration ought not neglect these factors, neither the coupling among them. In addition to this, their variation in the axial direction is significant not only in a general case but also for current membrane modules, so that part of the success of the predictions relies on the knowledge of this longitudinal “unsteady state”. Moreover, at a given axial position, the parameters in the cross-section of a module are subject to variations which are substantial, at least as regards the concentration and the velocity normal to the membrane; as a result, conceptions of the problem according to which the different parameters vary within a thin layer above the membrane only are not thorough.

In this scenario of notorious complexity, modeling is a promising approach, if not the unique, which allows comprehending the fundamentals governing the separation, quantifying its numerous parameters and phenomena and, eventually, predicting its results. We proposed to study the separation process by reverse osmosis numerically and pursued the development of a long-time approach of our research group, based among others in a convenient rationalization of parameters which had proved to be very adequate and insightful, and integrated the problematics of membrane transport to it. The numerical model and code solve the two-dimensional Navier-Stokes and mass transfer equations in dimensionless form subject to boundary conditions represented by the solution-diffusion model. Locally-varying hydrodynamics, pressure, concentration polarization, permeate flux and rejection rate were assumed.

We are henceforth equipped with a convenient and realistic simulation tool requiring a reduced set of determinable input parameters and are capable of simulating complex processes for which solution-diffusion membrane transport can be assumed, typically reverse osmosis and nanofiltration with tight membranes. The
Conclusions and Perspectives

Simulations enable to study the influence of all its inputs on averaged and local values like the permeate flux, rejection rate, pressure drop, concentration profiles including the membrane surface concentration, osmotic pressure, velocity field etc. The achievements and possibilities of such a comprehensive tool transcend those of traditional, simplified approaches currently employed and are therefore a promising substitute for them\textsuperscript{21}.

We studied the behavior of typical systems according to the value of solute permeability of the membrane. Briefly, \textit{reduced selectivity, or increased membrane solute permeability, enhances concentration polarization but counterbalances its effect by enhancing the permeate concentration concurrently, thus raising the permeate flux and, accordingly, reducing the pressure drop in the feed channel.}

Accordingly, \textit{the retentate is slowed down, its flow rate decreases and it gets more concentrated compared to the case with a more selective membrane.} It is interesting to note that membrane processes are studied from the point of view of the permeate only. It could be valuable to analyze it from the perspective of the concentrate, after all, if the target is a more concentrated permeate, employing a less selective membrane will result in a better separation.

A practical remark is that, within narrower ranges of variation typical for reverse osmosis or nanofiltration, the effects we have just explained are negligible (but detectable) in relation to the permeate flux. As a consequence, and as long as the permeate concentration is not being considered, most analyses can be performed with approximate values of solute permeability without major impact or adopt the assumption of total rejection. This is rather reassuring, for the solute permeabilities are frequently not known or are determined with significant incertitude. The accuracy of this uncoupled treatment seems to be ensured for different operating conditions as long as $B \leq 10^{-8}$ m·s$^{-1}$ (approximately).

Just as the permeate flux, the rejection rate is an important sought-after value. It is usually said that it increases with pressure (not \textit{because} of pressure!). We showed that this is only partially true and that a trade-off dependent on the inlet pressure exists between solute flux and permeate flux. The permeate concentration reaches a minimum, after which operation at higher pressure will result in lower or even negative rejection. In many practical cases, the minimal concentration is not attained.

\textsuperscript{21} The only exception to the “easily determinable” parameters may be the membrane solute permeability, commented some paragraphs below.
We compared the predictions of our model to experimental results from the literature in reverse osmosis and tight-nanofiltration and obtained good qualitative and quantitative results for modules of distinct geometry and dimensions, different operating conditions and solutes. The achievements of our model when dealing with so different cases are indicative of the advantages of modeling these processes by starting from their fundamentals and solving the basic equations by which they are governed. The cases where the agreement of permeate flux was worse or bad foreshadow possible ideas for future work. For summing up these and other perspectives, we would like to:

- Consider the concentration-dependent spatial variation of the solution properties, particularly the diffusion coefficient of the solute in the solvent and the solution viscosity. This is specially important for simulating solutions of high Schmidt, typical for macromolecular compounds. Variable coefficients can be implemented in the matrixes of coefficients of the numerical scheme;
- Evaluate the results obtained when another membrane transport model is implemented in the numerical model (e.g. Kedem-Katchalsky), currently under development in our group. Many questions are raised concerning the experimental determination of the additional parameters, but once they are know, we could simulate separations by nanofiltration. Studies advance in the description of electrostatic interactions and other mechanisms in NF, we believe that models much more fine and efficient than KK already dispose of enough parameters for certain applications;
- Integrate criteria and adapt the model for describing surface, reversible fouling/scaling, currently under development in our group in advanced stage;
- Integrate a solute transport mechanism to models in cylindrical geometry, currently under development in our group;
- Extend the model to three-dimensional geometry. This would allow studying wall effects qualitatively. Computational effort could become a concern (but not an impediment) and must be evaluated;
- Perform experiments with other solutes in addition to those tested in this thesis, currently under development in our group;
- Carry out experiments in a long and wide plate-and-frame or symmetric module (at least 1 m long, ideally much more), with empty flow channel, that is, without feed spacer. Combined with the absence of feed spacer,
Conclusions and Perspectives

the big dimensions enable to minimize edge effects and result in a (more) undisturbed concentration polarization layer, approaching the ideal problem corresponding at best to our models assumptions. Unfortunately, modules with all these characteristics do not seem frequent among experimentalists;

- Extend the model to multi-species separations.

The undisturbed slit is one of several existing configurations. Techniques for destabilizing the polarization layer are extremely frequent; the use of spacers is one of them. When simulating spacer-filled feed channels, the concept of hydraulic dispersion coefficient or, accordingly, effective Schmidt number, gives good results. It does not reproduce the mixing effect caused by the presence of the spacers, neither the additional pressure drop they generate, but reproduces the effect of the depolarization upon the permeate flux and rejection rates satisfactorily since the most important factor for them is estimating the concentration on the membrane surface, and not necessarily in the entire cross-section. This is already an important step, since the thorough modeling of spacer-filled channels is a very complex field.

We estimated Schmidt numbers empirically, a posteriori once the experimental results were available. A practical remark worth reminding is that the determination of the effective Schmidt value by this means must be carried out analyzing the permeate flux and rejection rates simultaneously. The recourse to CFD seems to be an inevitable path for studying the real physics of the problem and for determining the surface concentration. Large eddy simulation (LES) should allow notorious evolutions; if not for the excessive computational cost, direct numerical simulation (DNS) could also be evoked. The CFD problem itself should ideally include the permeate flux, determinant for the axial inhomogeneity of the problem. If not coupled to some model accounting for permeation, a prodigious part of the problem will have been solved, but not yet the whole situation.

Our simulations with spiral-wound modules enabled us to deepen our studies about the determination of membrane transport parameters.

The bench-scale experimental method we employed for the determination of permeability coefficients based on the osmotic-diffusive behavior of the system yielded utilisable results and allowed the calculation of water and salt permeabilities for reverse osmosis and nanofiltration membrane samples. The former were compared to the values obtained during the pressure-driven conditioning phase of the samples.
In osmotic-diffusive mode, the solute permeability coefficients showed to be dependent on the concentration difference $\Delta C$ across the membrane when very different $\Delta C$ were applied (up to a factor 35). This simple finding aimed at verifying the concentration-dependence of the solute permeability for, particularly, the chosen membranes and concentration ranges, which are widespread in today’s applications. It led to the observation that the water permeability was also very dependent on $\Delta C$ under the same conditions. Both variations may be explained in part by the modification of the transport properties according to membrane swelling/shrinkage, effects induced by concentration differences.

The water permeabilities under pressure were in most cases much higher than under osmosis, sometimes by one or even two orders of magnitude, yet they would be expected to be equivalent as suggested by the majority of transport models, which postulate the equivalence of hydrodynamic pressure and osmotic “pressure” (water activity gradient, actually) in relation to their capacity for promoting (or, alternatively, inhibiting) water flow.

In light of these remarks, it seems sound to think of a large contribution of convection to the water transfer in pressure-driven mode, even if the model’s assumptions are of solution-diffusion type, specially when reminding that the convective water flux has the same mathematical form as the solution-diffusion model, *i.e.* a linear law on $\Delta P$. If water convection increases, the solute passage to the permeate will also increase (not necessarily in the same proportion). If this is the case, the reversible modification of the membrane material by pressure should be evoked, particularly the possibility for more pores to be opened and to inner paths in the polymer to become connected, as sometimes discussed in the literature. Effects assimilable to those described by Staverman’s reflection coefficient would intervene and indicate the need for adapting the transport model. At the same time, the water and solute fluxes being so low and in opposite directions in osmosis-diffusion, mutual hindrance exerted by the solvent on the solute should not be excluded, neither a differential effect of the membrane itself on each flux; both effects would be reflected in the effective value of permeability calculated.

Anyway, the practical equivalence of the applied pressure $\Delta P$ and osmotic pressures $\Delta \pi$ for modeling the water flux as a function of $\Delta P - \Delta \pi$ in many barometric membrane separations is not denied, and the determination of the water permeability for such purposes should keep being done by measuring the filtrate flux obtained with pure water at various pressures. Whenever available, experimental
Conclusions and Perspectives

Osmotic pressure laws should be preferred because van’t Hoff’s is inaccurate at high concentrations (caused by concentration polarization).

For the prediction of rejection rates, the values of salt permeability may be approximated by our method. More tests are still needed to evaluate the experimental method and results more finely, but we obtained encouraging results. We compared them to the salt permeability values that best fitted the rejection rates obtained with the spiral-wound reverse osmosis module. These simulations revealed that the values we determined via osmosis-diffusion were not the best-fitting ones, but that they were not too far either. This can signify that the salt permeability is not completely modified by pressure, but only to a short extent. For that matter, the spacer-filled channel is closer to the ideal situation for the estimation of the solute permeability under the single effect of pressure; in the ideal case, concentration polarization virtually vanishes due to mixing and the effect of the hydrodynamic pressure upon the solute flux (effect exerted via the membrane) can be isolated.

For going further with these analyses, studies about the behavior of the membrane materials (and of the membranes) under pressure are of utmost importance, and would ideally be closely merged with those more specific to membrane transport. The determination of transport parameters is vital for accomplishing comprehensive process performance prediction. Reverse osmosis and many nanofiltration separations are concerned by small differences of rejection rate, and our simulations showed that not too big inaccuracies are enough for rejection rates to vary considerably. Actually, the determination of transport parameters for the purpose of determining rejection rates needs to fulfill two requirements: be fine (accurate) and not be detrimental to usability. Since “macroscopic” transport properties of membranes (e.g. permeabilities) are reflects of microscopic features (e.g. distribution of pores, free-volumes and chemical groups in the membrane matrix), the experimental method we propose could serve as a bridge between these two scales when it will be more knowledge-based.

We have some perspectives for the experimental method we proposed. We would like to do more experiments and have more results of water and salt permeability determined in osmosis-diffusion and in filtration, in order to compare them. It would be pertinent to compare the values of solvent and solute permeabilities determined by the same experimental method (e.g. ours) and with membranes of the same type, but conditioned at different pressures (e.g. 5 bar, 25 bar and 50 bar). We do expect the values to vary, however the sensitivity of the results to
the different experimental protocols still needs to be verified. The transferability of the membrane transport parameters obtained in osmosis-diffusion to pressure-driven mode seems to depend on this aspect too. Since we evoke the sensitivity of the transport parameters to the driving forces to which the membrane is subject, extreme initial concentration differences (e.g. 0.1 g·L⁻¹, 1 g·L⁻¹ and 50 g·L⁻¹ for aqueous sodium chloride could be tested. This will depend on the experimental means at disposal, in particular on the sensitivity of the analytical method used for monitoring the evolution of the concentrations.

In terms of improvements to our experimental method, we recommend to:

- Operate at constant temperature in order to avoid any influence on the flows and on the state of the membrane;
- Implement continuous (and non-destructive) measurement of concentrations and solution heights, so that more data will be available for the subsequent analysis;
- Reduce the cross-section of the compartments of each solution in order to observe a higher variation rate of the solution heights, but to an extent at which the pressure exerted by the concentrated liquid column remains negligible compared to $\Delta \pi$;
- Use a membrane sample with larger surface, in average more homogeneous spatially.

Finally, it would be of interest to model the experimental results from osmosis-diffusion with other transport models. In this case, more unknowns would need to be determined and, accordingly, the experiments complexified and diversified. Convection and diffusion could perhaps be quantified separately and, with them, the respective membrane transport properties.
APPENDIX A

Mathematical Formulation of Osmotic-Diffusive Experiments in the Kedem-Katchalsky Formalism

Following the same rationale from section 2.2.1, we write the solvent and solute flux equations in the KK-formalism from section 2.1.2.2:

\[
J_v(t) = -\sigma L_p^\dagger [C^+(t) - C^-(t)] \text{ where } L_p^\dagger = L_p iRT \tag{A.1}
\]

\[
J_s(t) = \omega [C^+(t) - C^-(t)] + (1 - \sigma)\bar{c}_s(t) \dot{J}_s(t) \text{ where } \omega = \omega iRT \tag{A.2}
\]

The mass balances for the dilute solution read:

\[
\frac{dV^{-}(t)}{dt} = -\sigma L_p^\dagger S[C^+(t) - C^-(t)] \tag{A.3}
\]

\[
C^-(t)\frac{dV^{-}(t)}{dt} + V^{-}(t)\frac{dC^-(t)}{dt} = \omega S[C^+(t) - C^-(t)] - (1 - \sigma)\bar{c}_s(t)\sigma L_p^\dagger S[C^+(t) - C^-(t)] \tag{A.4}
\]

And so:

\[
\frac{dC^-(t)}{dV^{-}(t)} = - \left[ \frac{\omega}{\sigma L_p^\dagger} + \sigma\bar{c}_s(t) + [C^-(t) - \bar{c}_s(t)] \right] \frac{1}{V^{-}} \tag{A.5}
\]

Integrating the previous equation under the approximation of constant \(\bar{c}_s(t) = \bar{c}_s\) and with the same initial conditions from Equation 2.59 \((C^{-}(0) = C_0^- = 0)\) and Equation 2.60 \((V^{-}(0) = V_0^-)\), we obtain the analogous of Equation 2.63 for the KK model:

\[
C^-(t) = \left[ \frac{\omega}{\sigma L_p^\dagger} - (1 - \sigma)\bar{c}_s \right] \left( \frac{V_0^-}{V^{-}(t)} - 1 \right) \tag{A.6}
\]

We could still write:

\[
C^-(t) = \left[ \frac{\omega}{L_p^\dagger_{app}} \right] \left( \frac{V_0^-}{V^{-}(t)} - 1 \right) \tag{A.7}
\]
APPENDIX A. Mathematical Formulation of Osmotic-Diffusive Experiments in the Kedem-Katchalsky Formalism

Where:

\[
\begin{bmatrix}
\omega^{\dagger} \\
L^{\dagger}_{app}
\end{bmatrix}
= \begin{bmatrix}
\omega^{\dagger} \\
\sigma L^{\dagger}
\end{bmatrix} - (1 - \sigma)\tilde{c}_{s}
\]

(A.8)

The subscript \textit{app} stands for “apparent”.

The determination of transport parameters by means of equation A.6 is not straightforward because of the introduction of two more parameters, \(\sigma\) and \(\tilde{c}_{s}\), the latter being moreover only a vague approximation of \(\tilde{c}_{s}(t)\) (itself doubtful).
APPENDIX B

Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

As mentioned in section 2.2.4.2, we present in the coming pages the measurements carried out in the concentrated and in the dilute solutions during the osmotic-diffusive experiments.

The error bars $\delta g$ for a generic dependent variable $g$, function $f$ of independent variables $p$ and $q$ (and others) associated with independent propagating uncertainties $\delta p$ and $\delta q$ (and others), were calculated by summing errors in quadrature Bally and Berroir [2008]:

$$g = f(p, q, ...)$$

$$\delta g = \sqrt{\left(\frac{\partial f}{\partial p}\right)^2 (\delta p)^2 + \left(\frac{\partial f}{\partial q}\right)^2 (\delta q)^2 + ...}$$

(B.1) (B.2)

Uncertainty when measuring heights was estimated at ±0.5 mm. It is due to parallax and to the position of the meniscus due to capilarity (±0.25 mm) and to the imprecision of the ruler used for the measurements (±0.25 mm).

The relative uncertainty during the conductivity measurements is indicated by the manufacturer of the conductivity meter as ±1 %.

As indicated by the manufacturer, temperature measurements are within ±0.5 °C.

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APPENDIX B. Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

Figure B.1: Experiments with the membrane BW30 starting with $C_0^+ = 1 \text{ g}\cdot\text{L}^{-1}$ and $C_0^- = 0$. 

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APPENDIX B. Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

Figure B.2: Experiments with the membrane BW30 starting with $C_{i0}^+ = 10 \text{ g L}^{-1}$ and $C_{0}^- = 0$. 
APPENDIX B. Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

Figure B.3: Experiments with the membrane BW30 starting with $C_{i0}^+ = 35 \text{ g L}^{-1}$ and $C_0^- = 0$. 
APPENDIX B. Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

Figure B.4: Experiments with the membrane NF270 starting with $C_0^+ = 1 \text{ g\cdot L}^{-1}$ and $C_0^- = 0$. 

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APPENDIX B. Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

Figure B.5: Experiments with the membrane NF270 starting with $C_0^+ = 10\text{ g L}^{-1}$ and $C_0^- = 0$. 
APPENDIX B. Time Evolution of the Heights, Concentrations and Temperatures of the Solutions during the Osmotic-Diffusive Experiments

Figure B.6: Experiments with the membrane NF270 starting with $C_0^+ = 35 \text{ g L}^{-1}$ and $C_0^- = 0$. 

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APPENDIX C

Model’s Boundary Conditions for a Kedem-Katchalsky Membrane

The following methodology was employed in section 3.2.4.1 for a wall of solution-diffusion-type.

We recap the volume and solute molar fluxes according to Kedem-Katchalsky model, Equations 2.15 (where $L_p = I_0^{-1}$) and 2.16:

$$ J_v = L_p(\Delta P - \sigma \Delta \pi) $$

$$ J_s = \omega \Delta \pi + (1 - \sigma) \tilde{c}_s J_v $$

The dimensionless Kedem-Katchalsky solute permeability is defined considering van’t Hoff’s osmotic pressure law (Equation 3.55):

$$ \omega^{*} \equiv \frac{\omega}{U_{in}} = \frac{iRT\omega}{U_{in}} $$

Table C.1 summarizes the parameters of the new problem whose permeable walls are Kedem-Katchalsky membranes:

<table>
<thead>
<tr>
<th>Dimensional parameters</th>
<th>$P_{in}$ $C_{in}$ $W_{in}$ $d$ $L$ $I_0^{-1}$ $\omega$ $\sigma$ $\rho_0$ $\mu_0$ $D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionless parameters</td>
<td>$Re_{in}$ (3.35) $Pe_{in}$ (3.59) $\alpha$ (3.38) $N_{osm}$ (3.80) $\tau$ (3.37) $\omega^{*}$ (C.1) $\sigma$</td>
</tr>
</tbody>
</table>

Table C.1: Eleven dimensional and seven dimensionless parameters describe the complete problem when a Kedem-Katchalsky mechanism is considered at the walls.

The solute conservation across the membrane reads:

$$ \omega^{*}[C(d, Z) - C_p(Z)] + (1 - \sigma)\tilde{c}_s(Z)U(d, Z) = U(d, Z)C_p(z) \Rightarrow $$

$$ C_p(Z) = \frac{\omega^{*}C(d, Z) + (1 - \sigma)\tilde{c}_s(Z)U(d, Z)}{\omega^{*} + U(d, Z)} $$

(C.2)
From which we see that the definition of $C_p(Z)$ depends on that of $\tilde{c}_s(Z)$. For instance:

\[
C_p(Z) = C(d, Z) \left[ \frac{\omega^\dagger}{U(d, Z)\sigma + \omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = C_p(Z) \tag{C.3}
\]

\[
C_p(Z) = C(d, Z) \left[ \frac{U(d, Z)(1 - \sigma) + 2\omega^\dagger}{U(d, Z)(1 + \sigma) + 2\omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = \frac{C_p(Z) + C(d, Z)}{2} \tag{C.4}
\]

\[
C_p(Z) = C(d, Z) \left[ \frac{U(d, Z)(1 - \sigma) + \omega^\dagger}{U(d, Z) + \omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = C(d, Z) \tag{C.5}
\]

As mentioned in section 2.1.2.2, suitable values of $\tilde{c}_s(Z)$ are usually comprised between $[C_p(Z) + C(d, Z)]/2$ and $C(d, Z)$. The previous equations read in dimensionless form:

\[
c_p(z) = c(1, z) \left[ \frac{\omega^\dagger}{u(1, z)\sigma + \omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = C_p(Z) \tag{C.6}
\]

\[
c_p(z) = c(1, z) \left[ \frac{u(1, z)(1 - \sigma) + 2\omega^\dagger}{u(1, z)(1 + \sigma) + 2\omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = \frac{C_p(Z) + C(d, Z)}{2} \tag{C.7}
\]

\[
c_p(z) = c(1, z) \left[ \frac{u(1, z)(1 - \sigma) + \omega^\dagger}{u(1, z) + \omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = C(d, Z) \tag{C.8}
\]

Equation 3.140, the solute mass balance on the membrane surface (which substitutes $(\partial c/\partial x) = u(1, z)c(1, z)Pe_{in}$ of Equation 3.86) is, accordingly:

\[
\frac{\partial c}{\partial x}(1, z) = \sigma Pe_{in} \ u^2(1, z)c(1, z) \left[ \frac{1}{u(1, z)\sigma + \omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = C_p(Z) \tag{C.9}
\]

\[
\frac{\partial c}{\partial x}(1, z) = \sigma Pe_{in} \ u^2(1, z)c(1, z) \left[ \frac{2}{u(1, z)(1 + \sigma) + 2\omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = \frac{C_p(Z) + C(d, Z)}{2} \tag{C.10}
\]

\[
\frac{\partial c}{\partial x}(1, z) = \sigma Pe_{in} \ u^2(1, z)c(1, z) \left[ \frac{1}{u(1, z) + \omega^\dagger} \right] \text{ for } \tilde{c}_s(Z) = C(d, Z) \tag{C.11}
\]

These concentration boundary conditions need to be discretized and adapted to
the form of Equation 3.109. For $\tilde{c}_s(Z) = C_p(Z)$:

$$
c_{j+1}^{(n+1)} = c_{j-1}^{(n+1)} + 2\Delta x P e_{in} \left[ \frac{\gamma_j^{(n+1)}}{\hat{u}_j^{(n+1)}(1 + \sigma) + \omega^*} \right] c_j^{(n+1)}
$$

$$
B_1(J) = P e_{in} \left\{ \frac{3}{2\Delta z} \hat{w}_j^{(n+1)} - \frac{2}{\Delta x} \left[ \frac{\gamma_j^{(n+1)}}{\hat{u}_j^{(n+1)}(1 + \sigma) + \omega^*} \right] \right\} + \frac{2}{(\Delta x)^2}
$$

For $\tilde{c}_a(Z) = [C_p(Z) + C(d, Z)]/2$:

$$
c_{j+1}^{(n+1)} = c_{j-1}^{(n+1)} + 2\Delta x P e_{in} \left[ \frac{2\gamma_j^{(n+1)}}{\hat{u}_j^{(n+1)}(1 + \sigma) + 2\omega^*} \right] c_j^{(n+1)}
$$

$$
B_1(J) = P e_{in} \left\{ \frac{3}{2\Delta z} \hat{w}_j^{(n+1)} - \frac{2}{\Delta x} \left[ \frac{2\gamma_j^{(n+1)}}{\hat{u}_j^{(n+1)}(1 + \sigma) + 2\omega^*} \right] \right\} + \frac{2}{(\Delta x)^2}
$$

And for $\tilde{c}_s(Z) = C(d, Z)$:

$$
c_{j+1}^{(n+1)} = c_{j-1}^{(n+1)} + 2\Delta x P e_{in} \left[ \frac{\gamma_j^{(n+1)}}{\hat{u}_j^{(n+1)} + \omega^*} \right] c_j^{(n+1)}
$$

$$
B_1(J) = P e_{in} \left\{ \frac{3}{2\Delta z} \hat{w}_j^{(n+1)} - \frac{2}{\Delta x} \left[ \frac{\gamma_j^{(n+1)}}{\hat{u}_j^{(n+1)} + \omega^*} \right] \right\} + \frac{2}{(\Delta x)^2}
$$

The new condition of permeation (which substitutes $u(1, z) = p(1, z) - N_{osm}c(1, z)$ of Equation 3.86) reads:

$$
u(1, z) = p(1, z) - \sigma N_{osm}[c(1, z) - c_p(z)]
$$

Similarly, it is discretized and adapted to the form of Equation 3.129.
APPENDIX C. Model’s Boundary Conditions for a Kedem-Katchalsky Membrane

For $\tilde{c}_s(Z) = C_p(Z)$:

$$
\left( \frac{3\Delta x}{4\Delta z} \right) w_0^{(n+1)} + \left( \frac{3\Delta x}{2\Delta z} \right) \sum_{j=1}^{j=J-1} w_j^{(n+1)} + p^{(n+1)} = \sigma N_{osm} \left[ \frac{\omega^+}{\hat{u}_j^{(n+1)} - \sigma + \omega^+} c_j^{(n+1)} \right]
+ \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right) + \sum_{j=1}^{j=J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2} w_j^{(n-1)} \right) \right]
\left( C.19 \right)
$$

$$
R2(J) = \sigma N_{osm} \left[ \frac{\omega^+}{\hat{u}_j^{(n+1)} - \sigma + \omega^+} c_j^{(n+1)} \right] + \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right)
+ \sum_{j=1}^{j=J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2} w_j^{(n-1)} \right) \right]
\left( C.20 \right)
$$

For $\tilde{c}_s(Z) = [C_p(Z) + C(d, Z)]/2$:

$$
\left( \frac{3\Delta x}{4\Delta z} \right) w_0^{(n+1)} + \left( \frac{3\Delta x}{2\Delta z} \right) \sum_{j=1}^{j=J-1} w_j^{(n+1)} + p^{(n+1)} = \sigma N_{osm} \left[ \frac{\omega^+}{\hat{u}_j^{(n+1)} - \sigma + \omega^+} c_j^{(n+1)} \right]
+ \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right) + \sum_{j=1}^{j=J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2} w_j^{(n-1)} \right) \right]
\left( C.21 \right)
$$

$$
R2(J) = \sigma N_{osm} \left[ \frac{\omega^+}{\hat{u}_j^{(n+1)} - \sigma + \omega^+} c_j^{(n+1)} \right] + \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right)
+ \sum_{j=1}^{j=J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2} w_j^{(n-1)} \right) \right]
\left( C.22 \right)
$$

And for $\tilde{c}_s(Z) = C(d, Z)$:

$$
\left( \frac{3\Delta x}{4\Delta z} \right) w_0^{(n+1)} + \left( \frac{3\Delta x}{2\Delta z} \right) \sum_{j=1}^{j=J-1} w_j^{(n+1)} + p^{(n+1)} = \sigma N_{osm} \left[ \frac{\omega^+}{\hat{u}_j^{(n+1)} - \sigma + \omega^+} c_j^{(n+1)} \right]
+ \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right) + \sum_{j=1}^{j=J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2} w_j^{(n-1)} \right) \right]
\left( C.23 \right)
$$

$$
R2(J) = \sigma N_{osm} \left[ \frac{\omega^+}{\hat{u}_j^{(n+1)} - \sigma + \omega^+} c_j^{(n+1)} \right] + \frac{\Delta x}{2\Delta z} \left( 2w_0^{(n)} - \frac{1}{2} w_0^{(n-1)} \right)
+ \sum_{j=1}^{j=J-1} \left[ \frac{\Delta x}{\Delta z} \left( 2w_j^{(n)} - \frac{1}{2} w_j^{(n-1)} \right) \right]
\left( C.24 \right)
$$

The rest of the coefficients in matrices 3.134 and 3.135 is not modified.
APPENDIX C. Model’s Boundary Conditions for a Kedem-Katchalsky Membrane

The new permeation velocity to be used in the convergence test is:

\[ U^{(k+1)} = p^{(n+1)} - \sigma N_{\text{osm}}[c_j^{(n+1)} - c_p(c_j^{(n+1)}; u_j^{(n+1)})] \] (C.25)

Problem solving follows as presented in sections 3.2.3 according to the algorithm in Figure 3.10.


B. Bernales, P. Guichardon, P. Haldenwang, and N. Ibaseta. Numerical modeling of concentration polarization and osmotic pressure effects in a 2-D membrane
channel: Application to reverse osmosis. Article submitted in 2014. [Cited on pages 108, 154, and 255.]


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SCIENTIFIC EVENTS

The works of this thesis have been presented in the scientific events listed below.

Refereed oral presentation with published conference proceedings:

Refereed oral presentations without published conference proceedings:


Refereed poster presentation with published conference proceedings:

Refereed poster presentations without published conference proceedings:


Non-refereed oral presentations without published conference proceedings:


G.H. Lopes*, P. Guichardon, N. Ibaseta, B. Bernales Chavez, P. Haldenwang. Prediction of permeate flux and rejection rate in reverse osmosis and nanofiltration membrane processes: numerical modelling of hydrodynamics and mass transfer coupling. 18e Colloque de Recherche Inter-Écoles Centrales (CRIEC), 2012, Marseille, France.

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I European Membrane Society
RÉSUMÉ ET MOTS-CLÉS

L’osmose inverse est un procédé de séparation qui occupe mondialement une place majeure relativement à ses nombreuses applications dans le domaine du traitement de l’eau (le dessalement, la production d’eau ultra pure, le traitement d’eaux municipales et industrielles) et de l’industrie agroalimentaire. Sa performance et son économie sont limitées par la polarisation de concentration, un phénomène réversible naturel engendré par un couplage complexe entre la pression, les conditions hydrodynamiques et le transfert de matière dans le canal d’alimentation du module membranaire. Interviennent aussi dans ce couplage l’influence de la composition de la solution traitée et des propriétés de transport de la membrane. La prédiction de la performance de ce procédé de séparation en termes de flux de perméat et de taux de rétention serait une avancée importante pour son dimensionnement, son contrôle et son optimisation.

La complexité du problème résidant dans la richesse des couplages ne peut être décrite par les approches phénoménologiques globales couramment développées dans le domaine des séparations membranaires. Pour avancer, nous avons choisi de modéliser la physique fondamentale inhérente à une séparation membranaire barométrique en phase liquide tout en incluant des hypothèses non-restrictives.

Pour un mode de séparation membranaire tangentiel, les équations de Navier-Stokes en écoulement laminaire stationnaire et l’équation de conservation du soluté sont résolues numériquement et simultanément dans un canal plan bidimensionnel. Deux cas particuliers de canaux seront étudiés : l’un, symétrique, est délimité par deux membranes, l’autre, asymétrique, comporte une paroi membranaire et une paroi imperméable. Le transport du solvant et du soluté à travers la membrane sont représentés à l’aide du modèle de solubilisation-diffusion. Réécrit à l’aide de variables adimensionnées et conformément aux hypothèses de Prandtl (selon lesquelles la diffusion axiale de quantité de mouvement et de matière est négligeable), le système est résolu en chaque point du maillage par un schéma de différences finies du deuxième ordre. Les concentrations, le flux de perméat, le taux de rétention, le champ de vitesses et la pression sont des exemples de paramètres qui peuvent être localement calculés.
La perméabilité de la membrane au soluté est un paramètre clé dont la détermination est particulièrement délicate. Nous avons ainsi développé une méthode expérimentale à l’échelle de la paillasse qui permet de déterminer les perméabilités au soluté et au solvant à partir d’expériences d’osmose-diffusion. Nous n’appliquons alors plus de pression sur la membrane mais une différence de concentration en soluté de part et d’autre de la membrane et suivons le transport du soluté à travers celle-ci. Les expériences ont été réalisées aussi bien sur des échantillons de membranes d’osmose inverse que de nanofiltration avec des solutions salines aqueuses. Cette méthode s’affranchit d’au moins deux inconvénients fréquemment rencontrés lors d’autres approches: la polarisation de concentration, dans le cas où les perméabilités sont déterminées en mode sous pression, et la non prise en compte du flux osmotique lorsque la détermination n’est pas réalisée sous pression.


Nos simulations mettent en évidence l’influence du transport à travers la membrane sur l’ensemble des résultats du procédé et le rôle primordial que joue la perméabilité dans les couplages complexes auxquels nous avons fait référence. La sensibilité de divers paramètres sur le flux de perméat et le taux de rétention, de même que la dépendance caractéristique du taux de rétention avec la pression appliquée, sont illustrées pour différentes valeurs de perméabilité au soluté. La comparaison de nos calculs aux résultats expérimentaux est bonne et encourageante. La détermination expérimentale des coefficients de perméabilité sous l’effet de la pression appliquée ou d’un gradient de concentration a été enrichissante. Les deux approches n’ont pas donné de résultats strictement équivalents mais les mêmes ordres de grandeurs sont obtenus pour la perméabilité au soluté. Nous avons identifié certaines limitations de notre modèle numérique et de notre méthode expérimentale de diffusion à l’échelle de la paillasse, et proposons des axes futurs de recherche. Le modèle et la méthode expérimentale de détermination de la perméabilité au soluté sont maintenant des outils prometteurs qui présentent une applicabilité immédiate.
RÉSUMÉ ET MOTS-CLÉS

dans le domaine des membranes.

MOTS-CLÉS: osmose inverse, nanofiltration, eau, dessalement, modélisation numérique, expérimental, polarisation de concentration, perméabilité, osmose, diffusion, membrane spiralée, taux de rétention, flux de perméat, modèle de solubilisation-diffusion
SYNTHÈSE DES TRAVAUX

CHAPITRE 1 Introduction

Les observations de Nollet sur la perméabilité, en 1748, auraient inauguré le champ d’études sur les membranes et les procédés membranaires. Pendant environ deux siècles, une série d’observations, de relations mathématiques et de considérations théoriques peu corrélées entre elles l’ont façonné davantage. Mais ce n’a été qu’à partir du développement des matériaux polymériques et plus particulièrement des membranes de Loeb et Sourirajan en 1962 que les séparations membranaires ont commencé à être utilisées de façon systématique pour diverses opérations à petite et grande échelles. Grâce à des avantages (niveaux de production et de sélectivité élevés, opération à température ambiante sans l’ajout de produits chimiques, facilité de mise en œuvre et d’opération, faibles impacts environnementaux) et malgré des inconvénients (limitation de performance engendrée par les phénomènes de colmatage et de polarisation de concentration, fragilité mécanique et faible résistance chimique des matériaux employés), les procédés membranaires sont actuellement au cœur de technologies de pointe pour des séparations en phases liquide, vapeur et gaz. Les séparations barométriques en phase liquide et plus particulièrement l’osmose inverse sont au cœur des préoccupations de la thèse. La nanofiltration est traitée de façon partielle. Le dessalement et le traitement des eaux, tout comme les secteurs agroalimentaire, pharmaceutique, électronique et biomédical en sont d’importants domaines d’application (Baker, 2004, pp. 1–14, 97; Böddeker, 1995; Drioli and Giorno, 2009, p. 21; Mulder, 1996, pp. 9–12; Strathmann, 2011, pp. 1–4).

L’osmose inverse fait intervenir des membranes capables de générer un flux de solvant élevé tout en maintenant une très haute sélectivité. Même les ions le plus petits sont fortement retenus par la membrane. La sélectivité est très variable en ce qui concerne les membranes de nanofiltration, moindre qu’en osmose inverse mais nettement plus élevée que pour d’autres séparations baromembranaires (ultrafiltration, microfiltration). Dans les deux cas, les couches sélectives des membranes sont le plus souvent fabriquées à partir de dérivées celluloses, des polyamides, des polyimides ou des polysulfones sulfonées tandis que les membranes entières

Le déroulement et les résultats des séparations sont fonctions des propriétés du mélange traité (solvants, solutés), de leurs interactions avec la membrane et également de la manière dont le procédé est conduit, c’est-à-dire, du choix des conditions opératoires et des spécificités des modules membranaires. S’ajoutent les effets des deux phénomènes limitants, la polarisation de concentration et le colmatage. Tous ces aspects sont entremêlés, ce qui rend difficile la modélisation du procédé et par conséquence sa simulation et la prédiction de ses résultats. Néanmoins, le besoin d’outils prédictifs est une réalité, et des avancées sur ce point sont nécessaires aussi bien d’un point de vue fondamental qu’appliqué.

En effet, la prédiction du flux de perméat (ou filtrat) et de sa concentration (ou taux de rétention), autrement dit, de la “productivité” et de la “qualité” atteintes par la procédé, est cruciale. Outre l’intérêt inhérent de ces deux paramètres, leur prédiction permettrait de réduire le nombre d’essais pilotes nécessaires à la mise au point du procédé (très nombreux dans ce domaine), de définir la surface membranaire et le nombre de passes, d’évaluer la performance de différentes membranes et modules membranaires ou alternativement de les optimiser, de définir les meilleures conditions opératoires etc.

Les approches phénoménologiques classiques utilisant des variables moyennées simplifient le problème. Ces dernières utilisent des corrélations empiriques et des coefficients de transport expérimentaux dépendants de l’application et du module membranaire utilisé. Elles ne sont donc ni générales, ni appropriées. Même si elles sont faciles à implémenter et suffisent pour les applications pour lesquelles elles ont été définies, d’autres outils sont nécessaires pour la simulation générale et la
SYNTHÈSE DES TRAVAUX

prédiction. De ce fait, nous proposons une autre approche et décidons d’étudier la physique fondamentale régissant le problème. Notre modélisation passe par l’utilisation d’un modèle numérique développé au sein de notre équipe et qui résout localement les équations de conservation de quantité de mouvement et de matière, désormais couplées à des modèles de transfert transmembranaire plus élaborés qui considèrent le transfert du soluté.

Le caractère prédictif du modèle est dépendant de la possibilité de connaître ses paramètres d’entrée. Parmi ceux-ci, la perméabilité de la membrane au soluté est délicate à déterminer. Une méthode “universelle” n’existant pas, nous proposons une méthode expérimentale de détermination de la perméabilité au soluté à l’échelle de la paillasse à partir de l’application d’un gradient transmembranaire de concentration. Cette méthode donne aussi comme résultat la valeur de la perméabilité au solvant.

L’utilisation d’outils de simulation pour des applications industrielles ou commerciales nécessite qu’ils soient validés, de même que les méthodes expérimentales associées. Le passage de l’échelle de la paillasse à l’échelle pilote et ensuite à l’échelle industrielle introduit des différences au niveau des résultats qu’il convient de confronter aux simulations afin d’estimer la pertinence de tout modèle. La validation de nos études à différentes échelles fait ainsi partie de ce travail.

Dans ce contexte, nous avons choisi d’étudier, en géométrie plane, le traitement de solutions aqueuses salines principalement par osmose inverse et subsidiairement par nanofiltration. Nos objectifs sont multiples:

• Modéliser numériquement et localement le couplage entre l’hydrodynamique et le transfert de matière dans un canal d’alimentation plan en filtration tangentielle et les propriétés de transport transmembranaire du solvant et du soluté;

• Déterminer expérimentalement à l’échelle de la paillasse la perméabilité du soluté à partir de l’évolution naturelle (sans appliquer de pression) d’un système en fonction du phénomène d’osmose et de la diffusion du soluté et vérifier l’influence de la concentration sur ce paramètre. Aussi, évaluer la pertinence des coefficients déterminés sans pression pour la simulation de procédés baromembranaires;

• Valider le modèle après comparaison avec nos propres valeurs expérimentales et des résultats tirés de la littérature;
SYNTHÈSE DES TRAVAUX

- Adapter notre approche au cas où le canal d’alimentation du module possède un espaceur qui joue le rôle de promoteur de turbulence;
- Mieux évaluer l’interaction entre les propriétés de transport de la membrane et le couplage de l’hydrodynamique avec le transfert de matière dans le canal d’alimentation.

Le colmatage n’est pas intégré à cette étude.


CHAPITRE 2  Transport Membranaire

Revue Bibliographique


Certains modèles traitent la membrane comme une “boîte noire” dans la mesure où ils ne postulent pas de mécanisme de transport et ne s’intéressent pas à la structure de la membrane. Leur but est d’exprimer des flux de matière en fonction de forces motrices. Les séparations membranaires étant des procédés hors équilibre, la Thermodynamique des processus irréversibles a servi de base à divers de ces modèles. Par exemple, pour un système à deux constituants (e.g. solvant et soluté),

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sa formulation linéaire inspirée des travaux d’Onsager mène à deux relations qui expriment le flux volumique total, \( q \), et le flux “chimique” ou “d’échange”, \( \chi \) (différence entre les vitesses du solvant et du soluté dans la membrane), en fonction de la différence de pression appliquée et de pression osmétique des deux côtés de la membrane, \( \Delta P \) et \( \Delta \pi \), et de coefficients phénoménologiques, \( L_p \), \( L_{p\pi} \) et \( L_\pi \) [Hwang, 2004; Pusch, 1977; Soltanieh and Gill, 1981; Strathmann, 2011, pp. 53–54]:

\[
q = L_p \Delta P + L_{p\pi} \Delta \pi \tag{SE.1}
\]

\[
\chi = L_{p\pi} \Delta P + L_\pi \Delta \pi \tag{SE.2}
\]

Les modèles de Kedem-Katchalsky et de Spiegler-Kedem sont classiques dans le domaine des membranes. Ils remplacent le flux chimique par le flux molaire de soluté, soluté, \( J_s \), une grandeur plus convenable expérimentalement, et assimilent le flux volumique total au flux volumique de solvant, \( J_v \). Ils considèrent encore qu’il peut y avoir un transport couplé du solvant et du soluté et ajoutent alors un troisième coefficient de transport, \( \sigma \), le coefficient de réflexion de Stavermann, qui varie de 0 pour une membrane totalement non-sélective à 1 pour une membrane qui n’admet pas de transport couplé. Kedem-Katchalsky formule le problème intégralement, tandis que Spiegler-Kedem opte pour une description locale. La plus ou moins grande dépendance des coefficients de transport par rapport aux forces motrices, notamment à la concentration, explique en partie ces différences. Leurs formulations respectives sont [Friedman and Meyer, 1981; Kedem and Katchalsky, 1958; Punzi and Muldowney, 1986; Soltanieh and Gill, 1981; Spiegler and Kedem, 1966; Staverman, 1951; Waniewski, 1994]:

\[
J_v = L_p (\Delta P - \sigma \Delta \pi) \tag{SE.3}
\]

\[
J_s = \omega \Delta \pi + (1 - \sigma) \tilde{c}_s J_v \tag{SE.4}
\]

\[
J_v = \mathcal{P}_v \left( \frac{dp^*}{dx} - \sigma \frac{d\pi^*}{dx} \right) \tag{SE.5}
\]

\[
J_s = \mathcal{P}_s \frac{dc^*}{dx} + (1 - \sigma) \tilde{c}_s J_v \tag{SE.6}
\]

Où \( \omega \) est la perméabilité de la membrane au soluté, \( \tilde{c}_s \) une concentration moyenne de soluté dans la membrane, et \( \mathcal{P}_v \) et \( \mathcal{P}_s \) sont des perméabilités locales au solvant et au soluté. L’exposant * symbolise des valeurs prises localement.
L’hypothèse de transport couplé est moins pertinente si la membrane est très perméable, car des membranes “denses”, comme celles d’osmose inverse, ce qui signifie que le flux de solvant peut être exprimé comme une fonction du gradient de pression effective $\Delta P - \Delta \pi$ seulement, et le flux de soluté du gradient de concentration $\Delta C$ exclusivement. Cette formulation correspond au très classique modèle de solubilisation-diffusion d’après lequel le transport à travers la membrane est assimilable au transfert de matière diffusif dans une phase unique. En faisant l’hypothèse d’équilibre local aux interfaces entre la membrane et les solutions à ses abords, il permet de décrire le transfert de matière à partir de paramètres de la solution extérieure à la membrane. Les flux molaires de solvant et de soluté, $N_v$ et $N_s$, s’expriment à l’aide de deux coefficients seulement, les perméabilités molaires au solvant, $A$, et au soluté, $B$. Ces paramètres contiennent notamment les coefficients de diffusion et de partage de chaque substance au sein de la membrane [Geise et al., 2011, 2014; Kocherginsky, 2010; Lonsdale et al., 1965; Paul, 1974, 2004; Paul and Elra-Lima, 1971; Pusch, 1986; Soltanieh and Gill, 1981; Wijmans and Baker, 1995].

\[
N_v = A(\Delta P - \Delta \pi) \quad \text{(SE.7)}
\]

\[
N_s = B(\Delta C) \quad \text{(SE.8)}
\]

Pour un même système, les valeurs de perméabilités ne sont pas immuables. Elles dépendent notamment de la concentration, de la pression et de la température. Les variations du coefficient de diffusion, de partage et de l’épaisseur de la membrane sont à l’origine de ces effets. Les différences au niveau de la réticulation et de la cristallinité du matériau de la membrane et de son hydation, souvent liées à des effets de charge, de constante diélectrique et de “volume libre” dans le polymère, sont des facteurs évoqués pour exprimer ces variations, de même que la compression mécanique, la modification de la porosité au sens large et la variation de la viscosité avec la température [Drazevic et al., 2014; Geise et al., 2011, 2013, 2014; Kedem and Freger, 2008; Merdaw et al., 2010; Paul, 2004; Soltanieh and Gill, 1981; Yasuda et al., 1968].

Il est courant, dans la littérature, de déterminer les perméabilités quand la membrane est sous pression. Dans ce cas, la permeabilité au solvant est la pente d’une représentation du flux de perméat en fonction de la pression transmembranaire quand du solvant pur est “filtré” [Hussain and Al-Saleh, 2014; Wright et al., 2005]. On pourrait dire que peu d’objections s’appliquent à cette méthode.
Pour ce qui est de la perméabilité au soluté, on utilise fréquemment des relations mathématiques non-prédictives de la littérature, dérivées des modèles ci-dessus avec différents degrés de simplification et d’hypothèses. Parmi ces dernières, on trouve la non prise en compte de la polarisation de concentration. Lorsque la polarisation de concentration est considérée, on a recours usuellement au modèle du film, commenté ultérieurement, et qui n’est pas sans critique [Lipp et al., 1994; Pusch, 1977, 1986; Soltanieh and Gill, 1981]. Pour illustration, notant $R$ le taux de rétention pour des conditions données et $R_\infty$ sa valeur quand $J_v \to \infty$. On a pour le modèle de solubilisation-diffusion:

$$\frac{1}{R} = \frac{1}{R_\infty} + \left( \frac{B}{R_\infty} \right) \frac{1}{J_v} \quad (SE.9)$$

La détermination des perméabilités peut aussi être effectuée quand la membrane n’opère pas sous pression. Dans ce cas, on sépare deux compartiments à différentes concentrations par une membrane et on laisse évoluer le système naturellement sous l’effet du gradient osmotique ou, autrement dit, des gradients de concentration de solvant et de soluté. Si le flux de solvant (flux osmotique) est négligeable ou n’est pas considéré, notant $S$ la surface de la membrane, considérant des volumes initiaux $V_0$ égaux dans les deux compartiments, la concentration initiale $C_0^+$ dans le compartiment plus concentré, et notant $C^-(t)$ la concentration du compartiment moins concentré à tout moment $t$, $B$ peut être obtenu de [Cussler, 2009; Geise et al., 2013; Yaroshchuk, 2010; Yasuda et al., 1968]):

$$\ln \left( \frac{C_0^+}{C_0^+ - 2C^-(t)} \right) = \left( \frac{2BS}{V_0} \right) t \quad (SE.10)$$

Alternativement, les déterminations dites d’“osmose directe” prennent en considération le flux osmotique. Elles sont clairement peu fréquentes dans la littérature. Normalement, les paramètres de transport dans la membrane sont ajustés aux expressions de flux de solvant et de soluté modélisés d’après différents modèles comme ceux ci-dessus. Les résultats révèlent des valeurs supérieurs, équivalents ou inférieurs à ceux déterminés sous pression en osmose inverse [Ghiu, 2003; Ghiu et al., 2002; Goosens and Van Haute, 1978].

Il convient de noter que les valeurs de perméabilité peuvent varier très fortement en fonction de l’échantillon de membrane (par exemple, 20% pour la perméabilité

$\text{Ray, 1994; Pusch, 1977, 1986; Soltanieh and Gill, 1981]$. Pour illustration, notant $R$ le taux de rétention\(^1\) pour des conditions données et $R_\infty$ sa valeur quand $J_v \to \infty$. On a pour le modèle de solubilisation-diffusion:

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La détermination des perméabilités peut aussi être effectuée quand la membrane n’opère pas sous pression. Dans ce cas, on sépare deux compartiments à différentes concentrations par une membrane et on laisse évoluer le système naturellement sous l’effet du gradient osmotique ou, autrement dit, des gradients de concentration de solvant et de soluté. Si le flux de solvant (flux osmotique) est négligeable ou n’est pas considéré, notant $S$ la surface de la membrane, considérant des volumes initiaux $V_0$ égaux dans les deux compartiments, la concentration initiale $C_0^+$ dans le compartiment plus concentré, et notant $C^-(t)$ la concentration du compartiment moins concentré à tout moment $t$, $B$ peut être obtenu de [Cussler, 2009; Geise et al., 2013; Yaroshchuk, 2010; Yasuda et al., 1968]):

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\(^1\) $R = 1 - C_p/C_{in}$ où $C_p$ est la concentration moyenne du perméat et $C_{in}$ la concentration de l’alimentation.
au solvant et 60 % pour la perméabilité au soluté [Schipolowski et al., 2006]).

Détermination des Perméabilités par des Essais d’Osmose-Diffusion

Nous avons mis en place un dispositif et une méthode de détermination expérimentaux de perméabilités par diffusion directe. Il s’agit d’un système idéalisé, isotherme qui fonctionne en régime transitoire. Il est composé de deux demi-cellules agitées qui sont séparées par une membrane (symétrique ou asymétrique indistinctement) de surface $S$, perméable au solvant et au soluté via un mécanisme de solubilisation-diffusion. Le dispositif est schématisé en Figure SF.1:

![Figure SF.1: Réprésentation schématique de la double cellule de diffusion agitée où deux solutions de différentes concentrations sont séparées par une membrane semiperméable.](image)

De part et d’autre de la membrane, nous allons appliquer une différence de concentration en soluté. S’établiront alors à contre-courant deux flux de résultantes unidimensionnelles. Le flux de soluté va entraîner une variation de la concentration en soluté dans chaque demi-cellule. Le flux de solvant se traduit par une variation, au cours du temps, du volume des solutions des compartiments, et aussi de leurs concentrations. Notant à nouveau $B$ la perméabilité au soluté et $I_0^{-1}$ la perméabilité volumique au solvant, utilisant les exposants $+$ et $-$ pour désigner les solutions concentrée et diluée respectivement (ou $\pm$ quand les deux sont considérées indistinctement), et exprimant les pressions osmotiques via la loi de van’t Hoff, les bilans volumique de solvant et molaire de soluté dans chaque compartiment s’écrivent, en négligeant l’effet de la colonne d’eau sur la solution concentrée:

$$\frac{dV^-(t)}{dt} = -(I_0^{-1})^+ S[C^+(t) - C^-(t)]$$  \hspace{1cm} (SE.11)

$$C^-(t) \frac{dV^-(t)}{dt} + V^-(t) \frac{dC^-(t)}{dt} = BS[C^+(t) - C^-(t)]$$  \hspace{1cm} (SE.12)
On notera que:
\[
\frac{dC^\pm(t)}{dV^\pm(t)} = \frac{dC^\pm(t)}{dt} / \frac{dV^\pm(t)}{dt} \quad \text{(SE.13)}
\]

Considérant les conditions initiales \( C^-(0) = C^-_0 = 0, \ V^-(0) = V^-_0, \ C^+(0) = C^+_0 \) et \( V^+(0) = V^+_0 \), la résolution de l’Équation SE.13 mène aux relations linéaires suivantes:

\[
C^-(t) = \frac{B}{(I_0^{-1})!} \left( \frac{V^-_0}{V^-(t)} - 1 \right) \quad \text{(SE.14)}
\]

\[
C^+(t) = \frac{B}{(I_0^{-1})!} \left( \frac{V^+_0}{V^+(t)} - 1 \right) + C^+_0 \left( \frac{V^+_0}{V^+(t)} \right) \quad \text{(SE.15)}
\]

Les pentes des Équations SE.14 et SE.15 expriment les rapports de perméabilité. Elles permettent ainsi d’accéder aisément à une certaine valeur caractéristique de la membrane.

L’obtention des perméabilités individuelles n’est pourtant possible qu’en résolvant le système d’équations différentielles linéaires du premier ordre réarrangé à partir de l’Équation SE.11 et de l’Équation SE.12, suivi d’un ajustement paramétrique:

\[
\frac{dV^-(t)}{dt} = (I_0^{-1})^! S \left( \frac{V^-(t)C^-(t)}{V^+_0 + V^-_0 - V^-(t)} + C^-(t) - \frac{V^+_0C^+_0 + V^-_0C^-_0}{V^+_0 + V^-_0 - V^-(t)} \right) \quad \text{(SE.16)}
\]

\[
\frac{dC^-(t)}{dt} = (I_0^{-1})^! S \left( \frac{C^+(t)[V^+_0C^+_0 + V^-_0C^-_0]}{V^-(t)(V^+_0 + V^-_0 - V^-(t))} + \frac{C^-(t)[V^+_0C^+_0 + V^-_0C^-_0]}{V^-(t)(V^+_0 + V^-_0 - V^-(t))} \right) + \frac{BS}{V^-(t)(V^+_0 + V^-_0 - V^-(t))} \quad \text{(SE.17)}
\]

Nous avons retenu un schéma de Runge-Kutta du quatrième ordre avec un pas de temps fixe [Abramowitz and Stegun, 1972, pp. 897] de 300 s implémenté sur Microsoft Excel 2010 pour résoudre ce système, et avons ajusté les valeurs de \( B \) et \( I_0^{-1} \).
SYNTHÈSE DES TRAVAUX

(a) Cellule de filtration comprimée entre deux blocs pressurisés
(b) Partie inférieure (gauche) et supérieure (droite) de la cellule.
(c) La surface conditionnée est vue en léger relief.

Figure SF.2: Unité de filtration tangentielle employée pour le conditionnement des membranes.

Résultats et Discussion

Les expériences ont été réalisées avec un échantillon de membrane d’osmose inverse plan, BW30 [Dow, a], et un de membrane de nanofiltration peu dense, NF270 [Hilal et al., 2005] (Dow Filmtec, États-Unis). Ces membranes ont été conditionnées au préalable avec l’aide de Pr. Marie-Pierre Belleville de l’Institut Européen des Membranes – IEM (Montpellier) en filtrant de l’eau pure à différentes pressions transmembranaires (PTM) jusqu’à environ 25 MPa à l’aide de l’unité de filtration montrée sur la Figure SF.2.

Les pentes moyennes retenues dans cette étude ont été calculées avec toutes les valeurs du cycle de pressions décroissantes, soit

\[ I_{0}^{-1} = 8.74 \times 10^{-12} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1} \]

pour la BW30 et

\[ I_{0}^{-1} = 5.72 \times 10^{-11} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1} \]

pour la NF270. Ce conditionnement a en outre montré que la pression transmembranaire maximale appliquée détermine fortement la valeur finale de perméabilité à l’eau, déduite des pentes illustrées par la Figure SF.3. Pour la BW30, l’augmentation de la porosité de la membrane avec la pression pourrait expliquer les perméabilités croissantes rencontrées pour des valeurs croissantes de pression. La compaction de la membrane NF270 sous l’effet de pressions croissantes, entraînant la réduction de son épaisseur, pourrait expliquer le comportement inverse rencontré pour la perméabilité de la membrane de nanofiltration [Kosutic et al., 2000; Pusch, 1986], de matrice plus “ouverte” (poreuse) et hydrophile que la membrane d’osmose inverse [Drazevic et al., 2014].

Les expériences de diffusion avec initialement des solutions aqueuses de chlorure de sodium d’un côté et de l’eau pure de l’autre ont été réalisées avec la double cellule de diffusion agitée qui nous a été prêtée par Olivier Boiron et Yannick...
SYNTHÈSE DES TRAVAUX

(a) Membrane d’osmose inverse BW30.  (b) Membrane de nanofiltration NF270.

Figure SF.3: Flux de perméat en fonction de la pression transmembranaire pendant le conditionnement des membranes.

Knapp de l’Institut de Recherche sur les Phénomènes Hors Équilibre – IRPHE (Marseille) et du matériel de Alain Kilidjian de l’École Centrale de Marseille. Elle est schématisée en Figure SF.4. Une photo est montrée en Figure SF.5.

Dix essais ont été réalisés, avec des durées allant de 4 à 16 jours environ. Conformément à la Figure SF.6, ils ont montré que le flux osmotique est plus marqué pour la membrane la plus sélective, celle d’osmose inverse, tandis que le flux de soluté est plus marqué pour la membrane la moins sélective, celle de nanofiltration.

Les valeurs des perméabilités ont été calculées par trois méthodes. La première (Osm.-diff.) consiste à ajuster les valeurs de $B$ et de $I_0^{-1}$ aux Équations SE.16 et SE.17 lors des expériences purement osmotiques et diffusives. L’autre (Mixte) comprend la détermination du rapport $B/I_0^{-1}$ par osmose et diffusion combiné et de la valeur de $I_0^{-1}$ par les mesures sous pression lors du conditionnement des membranes. La troisième méthode (Pure diff.) détermine $B$ à partir de l’Équations SE.10 (qui néglige le flux de solvant) en considérant $V_0 = V_0^−$. Toutes ces valeurs sont regroupées dans le Tableau ST.1.

Toutes les valeurs n’ont pas été reproductibles. Néanmoins, que ce soit pour $B$ ou pour $I_0^{-1}$, elles révèlent une nette décroissance avec $ΔC(t = 0)$, en accord avec les tendances générales discutées précédemment. On s’aperçoit aussi que les perméabilités à l’eau déterminées sous pression peuvent être très supérieures à celles déterminées sous gradient osmotique uniquement, parfois de deux ordres de grandeur. Ceci peut indiquer qu’elles ne décrivent pas le même phénomène physique. Aussi, on confirme que l’utilisation de l’Équation SE.10 a été appro-
Figure SF.4: Réprésentation schématique de la double cellule de diffusion. À gauche, vue frontale d’une demi-cellule dans la direction parallèle à la membrane. À droite, vue frontale du dispositif expérimental entier dans la direction perpendiculaire à la membrane. Schémas en échelle approximée.

Figure SF.5: Photo de la double cellule de diffusion employée pour la détermination des perméabilités membranaires prise au début d’une expérience. Le couvercle héberge les engrenages du système d’agitation. Les fils colorés servent à l’alimentation électrique.
SYNTHÈSE DES TRAVAUX

(a) Fraction d’eau transférée par osmose par rapport à la quantité initiale d’eau pure (b) Masse de chlorure de sodium qui a diffusé à travers la membrane.

Figure SF.6: Eau et sel transférés d’une solution à l’autre au cours du temps.

priée, comme espéré, seulement quand le flux osmotique est petit (avec la membrane de nanofiltration). Enfin, la méthode “mixte” a donné des résultats pour la plupart très différents des autres méthodes; étant donné qu’elle fait intervenir des coefficients déterminés sous des forces motrices différentes (sans ou avec $\Delta P$), cette méthode d’estimation est à considérer avec précaution.

Lors de la conception d’un procédé industriel, les valeurs de perméabilité dépendent des conditions locales qui sont fonction, entre autres, du phénomène de polarisation de concentration. Ce dernier résulte à son tour du couplage entre l’hydrodynamique et le transfert de matière dans le canal du module membranaire. La description de ce couplage est le thème du prochain chapitre. L’adéquation des perméabilités déterminées dans le présent chapitre sera évaluée dans le cadre de la simulation de l’osmose inverse décrit dans le Chapitre 4.
<table>
<thead>
<tr>
<th>Membrane</th>
<th>$\Delta C(t = 0)$ (g·L$^{-1}$)</th>
<th>Essai</th>
<th>$I_0^{-1}$ (m·Pa$^{-1}$·s$^{-1}$)</th>
<th>$B$ (m·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BW30</td>
<td>1</td>
<td>I</td>
<td>$6.5 \times 10^{-12}$</td>
<td>$8.7 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$1.1 \times 10^{-11}$</td>
<td>$8.7 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>I</td>
<td>$2.1 \times 10^{-12}$</td>
<td>$8.7 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$7.0 \times 10^{-13}$</td>
<td>$8.7 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>$7.4 \times 10^{-13}$</td>
<td>$8.7 \times 10^{-12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>$7.4 \times 10^{-13}$</td>
<td>$8.7 \times 10^{-12}$</td>
</tr>
<tr>
<td>NF270</td>
<td>1</td>
<td>I</td>
<td>$1.5 \times 10^{-12}$</td>
<td>$5.7 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
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</tr>
<tr>
<td></td>
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<td>I</td>
<td>$4.0 \times 10^{-13}$</td>
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<td></td>
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<td>II</td>
<td>$4.5 \times 10^{-13}$</td>
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<tr>
<td></td>
<td>35</td>
<td>I</td>
<td>$1.5 \times 10^{-13}$</td>
<td>$5.7 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Table ST.1: Valeurs de perméabilité calculées par trois méthodes
CHAPITRE 3  Modélisation de l’Hydrodynamique et du Transfert de Matière pour les Procédés de Séparation Membranaires

Revue Bibliographique

Compte tenu de la perméabilité, lorsque la solution traverse la membrane, le constituant le moins perméable, c’est-à-dire le soluté, est retenu d’avantage que le solvant. La concentration croissante au voisinage de la membrane implique un phénomène de rétrodiffusion d’une partie du soluté au sein de la solution, qui ne peut néanmoins contrer l’important apport de soluté par convection vers la surface membranaire. Par conséquence, une accumulation réversible de soluté a lieu spontanément sur la membrane. Dépendant des conditions hydrodynamiques, un profil de concentration s’établit dans le canal d’alimentation. Ce phénomène est nommé “polarisation de concentration”. Il a pour effets néfastes notamment la réduction de la pression effective du procédé et donc du flux de perméat, et l’augmentation du flux transmembranaire de soluté, donc la réduction du taux de rétention [Mulder, 1996, pp. 417–418; Strathmann, 2011, pp. 342–343; Baker, 2004, pp. 70, 241; Sablani et al., 2001].

La modélisation des phénomènes ayant lieu dans le canal de filtration peut être réalisée à l’aide de modèles pour la plupart unidimensionnels et qui considèrent toute variable comme étant constante le long du canal de filtration. Ces valeurs moyennées ne sont pas représentatives de toutes applications, mais fonctionnent au cas par cas. Ces modèles ont encore le mérite de mettre en évidence un certain nombre de phénomènes intervenant dans les filtrations membranaires, dont la polarisation de concentration. Les modèles du film, du gel, des résistances-en-série et le modèle de pression osmotique en sont les principaux représentants. Ils font appel à des coefficients de transfert et donc à des corrélations empiriques spécifiques à plus ou moins d’applications, ou à la notion de multiples résistances aux transferts dont les limites sont souvent difficiles à établir. Aussi, ils se concentrent sur le calcul du flux de perméat, ne traitant pas celui du taux de rétention [Belfort and Nagata, 1985; van den Berg et al., 1989; Cheryan, 1998, pp. 132–134; Gekas and Hallström, 1987; Geraldes and Afonso, 2006; Mulder, 1996, sec. VII.7.; Paris et al., 2002; Sablani et al., 2001; Strathmann, 2011, pp. 343–345, sec. 5.3.1.6; Velikovska et al., 2004].
SYNTHÈSE DES TRAVAUX

Une approche plus élaborée aboutit à des modèles locaux qui calculent toute variable en tout point du domaine étudié à partir de la résolution des équations générales de transfert de quantité de mouvement et de matière sous différentes hypothèses. Une grande variété d’approches existe en ce qui concerne la façon de traiter, par exemple, la pression transmembranaire, le profil de vitesse axiale, l’épaisseur de la couche de polarisation, la (non) variation spatiale de certains paramètres etc. [Ahmad and Lau, 2007; Belfort and Nagata, 1985; Bernales, 2013; Bernales et al.; Fletcher and Wiley, 2004; Geraldes et al., 2002; Ghidossi et al., 2006; Kim, 2007; Schwinge et al., 2004; Zhou et al., 2006].

Notre Approche

Nous présentons ici notre propre approche locale. Le modèle actuel s’inscrit dans la continuité d’un ensemble de vastes travaux menés dans notre équipe et depuis plusieurs années comme schématisés sur la Figure SF.7 [Bernales, 2013; Bernales et al.; Haldenwang, 2007; Haldenwang and Guichardon, 2011; Haldenwang et al., 2010; Lopes et al., 2014]. Nous ne synthétiserons ici que le modèle à son dernier stage de développement, entrepris dans le cadre de cette thèse.

Les paramètres physiques dont dépend le modèle sont les conditions opératoires $P_{in}$ et $W_{in}$, respectivement la pression transmembranaire et la vitesse axiale d’entrée; $C_{in}$, $\rho_0$, $\mu_0$ et $D_0$, respectivement la concentration de l’alimentation, sa masse volumique et sa viscosité dynamique et le coefficient de diffusion du soluté dans alimentation (les indices “in” et 0 dénotent des valeurs prises à l’entrée donc); $L$ et $d$, respectivement la longueur et une hauteur caractéristique du canal, égale à sa demi-hauteur s’il est symétrique (limité par deux membranes) ou à sa hauteur s’il est asymétrique (limité par une membrane et une paroi complètement imperméable); les perméabilité au soluté et au solvant, $B$ et $I^{-1}_0$. On note la coordonnée spatiale transversale dimensionnelle par $X$ et la longitudinale par $Z$, et les vitesses respectives par $U$ et par $W$; la concentration dans le canal par $C$ et dans le perméat par $C_p$ et la pression transmembranaire par $P$. Les deux configurations étudiées sont schématisées sur la Figure SF.8.

Dans notre modèle, toutes les variables sont adimensionnelles. Des nombres adimensionnels sont aussi introduits:

$$x = \frac{X}{d}, \quad z = \frac{Z}{L_{dc}}, \quad u = \frac{U}{U_{in}}, \quad w = \frac{W}{W_{in}}, \quad p = \frac{P}{P_{in}}, \quad c = \frac{C}{C_{in}} \quad \text{(SE.18)}$$
Figure SF.7: Schéma de l’approche progressive et unifiée développée dans notre équipe de recherche pour la modélisation de procédés de séparation membranaires barométriques en phase liquide. La littérature scientifique portant sur la perméation axialement uniforme d’un liquide pur a été revisitée. Puis, la filtration tangentielle de solvant pur dépendante localement de la pression a été modélisée. Ensuite, des solutions (un solvant avec un soluté) ont commencé à être considérées, c’est-à-dire la problématique (uniforme aussi bien que variable localement) de la polarisation de concentration combinée à l’osmose, et ce pour des membranes imperméables aux solutés (rétention totale). Cette hypothèse est désormais relaxée, la membrane présente une rétention partielle et ainsi les mécanismes de transport transmembranaire de soluté sont rajoutés au modèle, le mécanisme de perméation de solvant pouvant être aussi modifié. Des approches analytiques et numériques ont été privilégiées selon le cas. Des validations numériques et expérimentales ont également été réalisées à différents moments.

Où

\[ L_{de} = \frac{W_{in}d}{U_{in}} \quad U_{in} = I_{0}^{-1}P_{in} \]  

(SE.19)
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(a) Canal symétrique.

(b) Canal asymétrique.

Figure SF.8: Canaux d’alimentation soumis à une perméation de solvant dépendante localement de la pression et une perméation de soluté dépendante localement de la différence de concentration à travers la membrane. L’origine du système de coordonnées et la définition de $d$ changent d’un cas à l’autre. Schémas hors d’échelle ($d \ll L$).

Et encore:

\[
Re_{in}^I \equiv \frac{\rho_0 U_{in} d}{\mu_0} \quad Pe_{in} \equiv P_{in} \left( \frac{I_0^{-1} d}{D_0} \right) \quad \alpha \equiv \left( \frac{\mu_0 W_{in}^2}{I_0^{-1} P_{in}^2 d} \right)^{1/2} \quad (SE.20)
\]

\[
N_{osm} \equiv \frac{iRTC_{in}}{P_{in}} \quad \tau \equiv \frac{L}{L_{de}} \quad \beta^* \equiv \frac{B}{U_{in}} \quad (SE.21)
\]

Notons que $Pe_{in}$ est en réalité un nombre de Pécel et résulte du produit de $Re_{in}^I$ par le nombre de Schmidt à l’entrée, $Sc = \mu_0 \rho_0 / D_0$. Les équations de Navier-Stokes se réduisent au bilan de quantité de mouvement dans la direction axiale seulement et les termes de diffusion axiale de quantité de mouvement sont négligés en accord avec l’approximation de Prandtl [Haldenwang, 2007; Haldenwang et al., 2010; Schlichting, 1968]. Étendant ces considérations à l’équation de conservation
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du soluté, le système d’équations à résoudre est:

\[ \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0 \quad \text{(SE.22)} \]

\[ \frac{\partial p}{\partial x} = 0 \quad \text{(SE.23)} \]

\[ Re_{in} \left( u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} \right) = -\frac{1}{\alpha^2} \frac{\partial p}{\partial z} + \frac{\partial^2 w}{\partial x^2} \quad \text{(SE.24)} \]

\[ Pe_{in} \left( u \frac{\partial c}{\partial x} + w \frac{\partial c}{\partial z} \right) = \frac{\partial^2 c}{\partial x^2} \quad \text{(SE.25)} \]

Dans le domaine \( \omega = \{0 < x < 1\} \times \{0 < z < \tau\} \), il est soumis aux conditions aux limites:

\[ u(1, z) = p(1, z) + N_{osm}[c(1, z) - c_p(z)] \quad u(0, z) = 0 \]

\[ w(1, z) = 0 \quad \frac{\partial w}{\partial x}(0, z) = 0 \ (\text{sym.}) \text{ ou } w(0, z) = 0 \ (\text{asym.}) \]

\[ \frac{\partial c}{\partial x}(1, z) = Pe_{in} u^2(1, z)c(1, z) \left[ \frac{1}{\beta^* + u(1, z)} \right] \quad \frac{\partial c}{\partial x}(0, z) = 0 \quad \text{(SE.26)} \]

Ce faisant, le modèle de solubilisation-diffusion est retenu pour décrire le transport à travers la membrane (mathématiquement, cela ne concerne que des conditions aux limites).


Étude par Simulation

Nous avons souhaité étudier l’impact de la sélectivité de la membrane, particulièrement de la valeur de perméabilité au soluté, sur les résultats du procédé et sur l’hydrodynamique et le transfert de matière dans le canal. Le cas du traitement de solutions aqueuses de chlorure de sodium de \( C_{in} = 1 \ \text{g}\cdot\text{L}^{-1} \) jusqu’à \( C_{in} = 35 \ \text{g}\cdot\text{L}^{-1} \) à 25°C entre \( P_{in} = 1.5 \times 10^5 \ \text{Pa} \) et \( P_{in} = 60 \times 10^5 \ \text{Pa} \) (la pression manométrique du côté du perméat vaut zéro) et pour \( W_{in} = 0.1 \ \text{m}\cdot\text{s}^{-1} \), dans un canal symétrique limité par des membranes d’osmose inverse de \( I_0^{-1} = 5 \times 10^{-12} \ \text{m}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1} \) pour lequel \( d = 0.5 \ \text{mm} \) et \( L = 6 \ \text{m} \) a été simulé. Cette étude a montré que le flux de
perméat augmente au fur et à mesure que $B$ augmente (Figure SF.9).

![Figure SF.9: Évolution du flux de perméat adimensionnel en fonction de la pression d’entrée adimensionnelle pour trois valeurs de concentrations et six valeurs de perméabilité au solute. $Pe_{av}$ est le nombre de Péclet calculé avec le flux de perméat moyen.](image)

Cette augmentation ne saurait être expliquée par une réduction du phénomène de polarisation de concentration quand des membranes plus perméables au soluté sont utilisées car ce phénomène est intensifié à $B$ plus élevé. En réalité, l’augmentation de la concentration du perméat à $B$ plus élevé est telle que la différence de concentration en soluté des deux côtés de la membrane est amoindrie, et donc la pression effective, $\Delta P - \Delta \pi$, est plus grande pour $B$ plus grand. Cela a également l’effet de réduire la perte de charge dans le canal de filtration à cause de la diminution de débit qui y a lieu. Cette réduction de perte de charge induit une augmentation de la pression transmembranaire $\Delta P$ (effet beaucoup moins prononcé que celui dû à la réduction de $\Delta \pi$). On aurait pu raisonner en considérant le rétentat. Lorsque $B$ augmente, le débit de rétentat diminue et le rétentat se concentre davantage. La Figure SF.10 illustre ces idées en montrant des profils transversaux à différentes positions axiales le long du canal pour une solution de $C_m = 10 \text{g·L}^{-1}$ à $P_m = 30 \times 10^5 \text{Pa}$ pour 3 valeurs de perméabilité au soluté: $B = 0 \text{m·s}^{-1}$, $B = 10^{-8} \text{m·s}^{-1}$ et $B = 10^{-6} \text{m·s}^{-1}$ (les deux premières valeurs donnent des valeurs pratiquement superposables). L’évolution des profils avec $z$ s’explique du fait de la perméation du solvant le long du canal et de l’intensification du phénomène de polarisation de concentration (en partie liés). La variable $z$ y représente une valeur adimensionnée par la longueur du canal,
La valeur de $B$ joue également un rôle sur la concentration du perméat (taux de rétention) bien évidemment, qui augmente avec $B$. Nous montrons encore que la concentration du perméat a une dépendance non-monotone avec la pression appliquée et nous voyons apparaître un minimum. L’augmentation de la pression diminuera la concentration du perméat, ce qui correspond à une observation expérimentale fréquente, tant que ce minimum n’est pas atteint. Ensuite, en revanche, elle augmentera jusqu’à éventuellement dépasser la concentration d’alimentation (rétention négative). En effet, tant que le minimum n’est pas atteint, le flux de perméat augmente avec la pression dans des proportions plus importantes que l’augmentation du flux de soluté. Nous observons donc un effet
de dilution et le taux de rétention augmente avec la pression. Pour des pression bien supérieures, la polarisation de concentration devient prépondérante et le flux de soluté est trop important par rapport à la désormais faible augmentation de flux de perméat. Il en résulte une augmentation de concentration du perméat en soluté. Ces conclusions sont illustrées par la Figure SF.11.

Figure SF.11: Évolution de la concentration du perméat adimensionnelle en fonction de la pression d’entrée adimensionnelle pour 3 concentrations et 6 valeurs de perméabilité au soluté.

Que ce soit pour le flux de perméat ou pour le taux de rétention, les effets mentionnés ne deviennent significatifs qu’à partir de valeurs de B supérieures à $B = 10^{-8} \text{ m.s}^{-1}$, sauf si des taux de rétention très fins sont à prédire (troisième voire quatrième cases décimales par exemple). Aussi, pour des perméabilités au soluté inférieures à cette valeur, les résultats sont peu sensibles à $B$ et l’estimation du flux de perméat avec l’hypothèse d’une rétention totale présentera peu d’erreurs.

Une étude semblable étudiant l’influence de la perméabilité prise égale à $I_0^{-1} = 5 \times 10^{-11} \text{ m.Pa}^{-1}.\text{s}^{-1}$ (caractéristique de la nanofiltration) et à $I_0^{-1} = 5 \times 10^{-12} \text{ m.Pa}^{-1}.\text{s}^{-1}$ (caractéristique de l’osmose inverse), a montré l’effet qu’a sur tous les paramètres du procédé l’augmentation du flux de perméat résultante d’un $I_0^{-1}$ plus grand. Notamment, en valeurs adimensionnelles, la couche de polarisation de concentration est encore plus importante et la réduction du flux de perméat plus sévère.

Dans le prochain chapitre, nous appliquons notre modèle à divers cas expérimentaux réels.
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CHAPITRE 4  Validation du Modèle et Comparaison avec des résultats Expérimentaux

Modules Membranaires Plans

Nous présentons et commentons succinctement l’application du modèle à quelques résultats expérimentaux tirés de la littérature et obtenus avec des modules plans.

Flux de Perméat

La Figure SF.12 est issue des comparaisons des résultats numériques aux expériences de Ahmad and Lau [2007] avec différentes solutions salines et une membrane de nanofiltration pour laquelle $I_0^{-1} = 4.72 \times 10^{-11}$ m·Pa$^{-1}$·s$^{-1}$ dans un canal asymétrique pour lequel $L = 25.5$ cm, $d = 0.1$ cm et la largeur $w_l = 2.5$ cm. Le modèle décrit bien les tendances d’augmentation du flux de perméat avec la vitesse axiale et la pression transmembranaire. Les erreurs entre simulations et valeurs expérimentales de flux de perméat sont satisfaisantes, à $\pm 15\%$ pour la plupart.

Les expériences de Zhou and Song [2005] avec une membrane d’osmose inverse de $I_0^{-1} = 4.26 \times 10^{-12}$ m·Pa$^{-1}$·s$^{-1}$ dans un canal asymétrique pour lequel $L = 19.1$ cm, $d = 0.171$ cm et de largeur $w_l = 14$ cm sont comparées sur la Figure SF.13 aux flux de perméat simulés. Les expérimentateurs ont traité des solutions aqueuses de chlorure de sodium à différentes concentrations. Les erreurs relatives entre simulations et valeurs expérimentales du flux de perméat varient dans des plages allant de $3\%$ à $27\%$ (valeurs absolues). Les écarts seraient dus en grande partie aux estimations imprecises de $B$ réalisées par les expérimentateurs, qui ont négligé l’effet de la polarisation de concentration. Des solutions aqueuses de Na2SO4, de sucre et de polyéthylène glycol de 1000 g/mol (PEG1000) ont été traitées par Geraldes et al. [2002] avec une membrane de nanofiltration de $I_0^{-1} = 1.4 \times 10^{-11}$ m·Pa$^{-1}$·s$^{-1}$ dans un canal asymétrique pour lequel $L = 20$ cm, $d = 0.2$ cm et $w_l = 3$ cm. Les comparaisons des flux de perméat obtenus dans des zones délimitées et séparées le long du canal (collecteurs) avec nos résultats numériques sont illustrées par la Figure SF.14 pour trois valeurs de Reynolds axial ($W_{in}$). Les prédictions pour le sel sont très précises (entre $-3\%$ et $7.5\%$ d’erreur). Les erreurs sont inférieures à $20\%$ pour le sucre. En ce qui concerne le PEG1000, elles montent jusqu’à $72.5\%$, une valeur très élevée. De telles erreurs
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(a) Sucrose, $C_{in} = 2 \text{ g·L}^{-1}$

(b) MgSO$_4$, $C_{in} = 5 \text{ g·L}^{-1}$

(c) Na$_2$SO$_4$, $C_{in} = 2 \text{ g·L}^{-1}$.

Figure SF.12: Comparaison aux résultats expérimentaux de flux de perméat présentés par Ahmad and Lau [2007]. $U_{av}$ est le flux de perméat moyen.

s’expliqueraient par la diminution du coefficient de diffusion du soluté dans la solution avec la concentration pour une solution dont le coefficient de diffusion est déjà beaucoup plus petit que pour les autres cas. Ces effets conduisent à une polarisation de concentration aggravée qui n’est pas considérée par notre modèle actuel, lequel assume $\rho_0$, $\mu_0$ et $D_0$ constants, résultant ainsi en une surestimation du flux de perméat.

Taux de rétention

Le principal facteur d’erreur entre les simulations de taux de rétention et les valeurs expérimentales est la valeur de perméabilité au soluté. Sa détermination com-
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Figure SF.13: Comparaison aux résultats expérimentaux de flux de perméat de Zhou and Song [2005]. $U_{av}$ est le flux de perméat moyen.

porte très souvent des incertitudes. Ahmad and Lau [2007] ont fait appel à une démarche semi-expérimentale pour les déterminer, où des données expérimentales de rétention apparente sont intégrées à un modèle numérique qui en extrait des propriétés de transport membranaire en tenant compte de la polarisation de concentration. Les comparaisons avec nos prédictions montrent un bon accord dans ce cas, comme en témoigne la Figure SF.15. Les valeurs de perméabilité déterminées par Zhou and Song [2005] sans tenir compte de la polarisation de concentration entraînent des erreurs beaucoup plus importantes lorsque les conditions opératoires sont favorables à une polarisation plus intense, comme on peut le voir sur la Figure SF.16.

Modules Membranaires Spiralés

Un nombre important de modules membranaires contiennent des “espaceurs” dans le canal d’alimentation, c’est-à-dire une structure en forme de grille dont l’objectif est à la fois de donner forme au canal d’écoulement et de réduire l’intensité de la polarisation de concentration en intensifiant les tourbillonnements (mélange) dans le canal. Ceci à comme objectif ultime d’augmenter les coefficients de transfert de

\[ \text{La rétention intrinsèque est définie par rapport à la concentration sur la surface de la membrane, et non pas à la concentration d’alimentation.} \]
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(a) Na$_2$SO$_4$ solution, collecteur 1.  (b) Na$_2$SO$_4$ solution, collecteur 2.  (c) Solution de Na$_2$SO$_4$, collecteur 3.

(d) Solution de sucrose, collecteur 1.  (e) Solution de sucrose, collecteur 2.  (f) Solution de sucrose, collecteur 3.

(g) Solution de PEG1000, collecteur 1.  (h) Solution de PEG1000, collecteur 2.  (i) Solution de PEG1000, collecteur 3.

Figure SF.14: Comparaison aux résultats expérimentaux de flux de perméat de Geraldes et al. [2002]. $U_{av}$ est le flux de perméat moyen.
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(a) Sucrose, \( C_{in} = 2 \text{ g L}^{-1} \)

(b) \( \text{MgSO}_4 \), \( C_{in} = 5 \text{ g L}^{-1} \)

(c) \( \text{Na}_2\text{SO}_4 \), \( C_{in} = 2 \text{ g L}^{-1} \).

Figure SF.15: Comparaison aux résultats expérimentaux de taux de rétention intrinsèques présentés par Ahmad and Lau [2007].

matière. Les espaceurs sont présents dans certains modules plans, mais c’est dans les modules spiralés, représentés dans la Figure SF.17, que leur usage est le plus répandu [Da Costa et al., 1991; Dow, d; Ghidossi et al., 2006; Schock and Miquel, 1987; Schwinge et al., 2004].

La modélisation précise des transferts dans un canal contenant un espaceur est un sujet à part entière de très grande complexité et qui ne rentre pas dans le cadre de cette thèse. En effet, elle doit intégrer, parmi d’autres, l’effet de la polarisation de concentration perturbée et amoindrie par le mélange causé par l’espaceur. Une approche alternative proposée par Zhou et al. [2006] reproduit la réduction de la concentration à la surface de la membrane par l’utilisation d’un “coefficient de dispersion hydraulique”, \( D_{HD} \), au lieu du coefficient de diffusion moléculaire \( D_0 \)
Figure SF.16: Comparaison aux résultats expérimentaux de taux de rétention de Zhou and Song [2005].

Figure SF.17: Illustration d’un module spiralé. Images adaptées de Baker [2004, p. 144].

tel que $D_{HD} > D_0$. Cela revient à simuler une rétrodiffusion de soluté accrue vers le sein de l’écoulement, mais n’implique aucunement que les profils simulés correspondent aux réalités physiques. On peut transposer le principe de $D_{HD}$ au nombre de Schmidt; on parlera dans ce cas d’un nombre de Schmidt apparent, $Sc_{app}$ [Lopes et al., 2014].

Nous avons appliqué ce concept à nos propres expériences menées dans le hall pilote de Génie des Procédés de l’Ecole Centrale de Marseille sur l’installation pilote de la Figure SF.18 (PIGNAT OSM/2000, France), laquelle comporte des modules
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spiralés de 1 m de longueur et de diamètre 9.9 cm. Des solutions aqueuses de chlorure de sodium ont été traitées à $P_{in} < 25 \times 10^5$ Pa et 25 °C avec la membrane d’osmose inverse BW30-4040 (Dow Filmtec, États-Unis) [Dow, a] (la même de l’échantillon plan utilisé dans le Chapitre 2).

Figure SF.18: Pilote pour modules membranaires spiralés utilisé lors de nos expériences.

Dans un tel cas, le modèle ne peut plus être envisagé comme un outil prédictif. Son application a montré qu’un nombre de $Sc_{app}$ à partir de 3 ou 4 fois plus petit que le nombre de Schmidt moléculaire permet de reproduire les comportements du flux de perméat et du taux de rétention simultanément pour diverses conditions opératoires. On a aussi confirmé que, en effet, le flux de perméat est peu sensible à la perméabilité au soluté, mais que $B$ demeure tout de même déterminant pour le taux de rétention. Nous illustrons par la Figure SF.19 cette analyse pour une solution de concentration $C_{in} = 10 \text{ g·L}^{-1}$.

Des expériences réalisées à d’autres concentrations ont permis d’ajuster les valeurs de $B$ pour décrire au mieux les courbes, notamment celles du taux de rétention. Ces valeurs ont été comparées aux valeurs de $B$ obtenues par les deux premières méthodes présentées au Chapitre 2 (la méthode des expériences osmotiques et diffusives et la méthode mixte obtenue à partir des rapports $B/I_0^{-1}$ calculés en

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Figure SF.19: Résultats expérimentaux et numériques pour l’eau pure et une solution aqueuse de NaCl ($C_{in} = 10 \text{g} \cdot \text{L}^{-1}$) à $W_{in} = 0.11 \text{m} \cdot \text{s}^{-1}$ pour trois valeurs différentes de $B$. $I_0^{-1} = 7.13 \times 10^{-12} \text{m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$, $i = 2$ et $R$ est la constante universelle des gaz. $B/I_0^{-1}iRT$ a les unités mol$\cdot$m$^{-3}$, $Pe_{av}$ est le nombre de Péclet calculé avec le flux de perméat moyen, et $R_{av}$ le taux de rétention moyen.

osmose-diffusion et combinée à la valeur de $I_0^{-1}$ déterminée sous pression lors de l’essai pilote avec le module spiralé). L’ensemble des valeurs des perméabilités sont présentées dans le Tableau ST.2 où $C_{av}$ est la concentration moyenne (axialement) sur la membrane spiralée, une valeur simulée et plus appropriée à la comparaison avec les différences de concentration initiale utilisées dans le Chapitre 2.

Les valeurs de $B$ ajustées pour la membrane spiralée sont différentes de celles déterminées en osmose-diffusion, bien qu’elles aient le même ordre de grandeur. La méthode mixte donne des valeurs jusqu’à un ordre de grandeur supérieures aux valeurs ajustées, ce qui pourrait indiquer que les mécanismes de transport dans la membrane sans pression ou sous pression, c’est-à-dire engendrés par $\Delta P$ ou $\Delta \pi$ isolément, sont différents.

Nous avons également comparé les simulations à des expériences menées avec des
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solutions aqueuses de MgSO$_4$ et de Na$_2$SO$_4$ avec le module spiralé de nanofiltration peu dense NF270-4040 (Dow Filmtec, États-Unis) [Dow, c]. Même si cette membrane est assez poreuse, ces solutés ont des masses et tailles moléculaires élevées, raison pour laquelle on pourrait imaginer que le modèle de solubilisation-diffusion soit capable de reproduire les résultats du procédé de séparation. L’ajustement de la valeur du $Sc_{app}$ et de $B$ a bien permis de reproduire les flux de perméat et les taux de rétention. Nous ne pouvons pourtant pas affirmer que le mécanisme physique prépondérant a été effectivement du type solubilisation-diffusion.
<table>
<thead>
<tr>
<th>$C_{in}$ (g·L$^{-1}$)</th>
<th>$C_{av}^M$ (g·L$^{-1}$)</th>
<th>$B$ (m·s$^{-1}$)</th>
<th>$\Delta C(t = 0)$ (g·L$^{-1}$)</th>
<th>$B$ (m·s$^{-1}$)</th>
<th>$\Delta C(t = 0)$ (g·L$^{-1}$)</th>
<th>$B$ (m·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>$\leq$ 2.4</td>
<td>3.5 $\times$ 10$^{-8}$</td>
<td>1.0</td>
<td>$5.6 \times 10^{-8} - 9.0 \times 10^{-8}$</td>
<td>1.0</td>
<td>6.4 $\times 10^{-8}$</td>
</tr>
<tr>
<td>5.2</td>
<td>$\leq$ 7.7</td>
<td>3.5 $\times$ 10$^{-8}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10.0</td>
<td>$\leq$ 13.0</td>
<td>8.8 $\times$ 10$^{-8}$</td>
<td>10.0</td>
<td>3.6 $\times 10^{-8}$</td>
<td>10.0</td>
<td>1.3 $\times 10^{-7}$</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>35.0</td>
<td>1.5 $\times 10^{-8} - 1.9 \times 10^{-8}$</td>
<td>35.0</td>
<td>1.6 $\times 10^{-7} - 1.9 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table ST.2: Valeurs de perméabilité au soluté et les respectives concentrations.
Conclusions et Perspectives

La modélisation des procédés membranaires d’osmose inverse et de nanofiltration ne peut faire l’économie de la description rigoureuse du couplage complexe existant entre les propriétés de transport de la membrane, les propriétés du mélange à traiter, les conditions de pression et hydrodynamiques ainsi que de la polarisation de concentration dans le canal d’alimentation. Nous nous sommes intéressés à ce problème et avons choisi de le modéliser numériquement en poursuivant une approche propre à notre équipe de recherche. Considérant l’hydrodynamique, la pression, la polarisation de concentration, le flux de perméat et le taux de rétention des grandeurs variables localement, ce modèle et le code numérique qui s’y rapporte résolvent les équations de Navier-Stokes et de conservation de la masse d’une espèce dans le canal d’alimentation et les couplent à des conditions aux limites représentant des membranes du type solubilisation-diffusion. Désormais, on dispose d’un outil de simulation pour l’osmose inverse et les membranes de nanofiltration denses qui utilise un ensemble restreint de paramètres d’entrée dont la détermination est immédiate, excepté pour la perméabilité au soluté. Cet outil permet de prédire des valeurs locales et moyennes de grandeurs importantes telles que le flux de perméat, le taux de rétention, la chute de pression, les profils de concentration, le champ de vitesses, la concentration et le débit de rétentat etc., excédant ainsi les possibilités atteintes par les modèles classiques. Il montre de ce fait un potentiel intéressant pour remplacer ces derniers. La comparaison des simulations numériques à des résultats expérimentaux tirés de la littérature et à d’autres réalisés par nos soins a démontré l’efficacité du modèle tant qu’il est employé dans les limites des considérations qu’il présuppose.

Le transport à la membrane, et plus particulièrement la perméabilité au soluté, est une dimension fondamentale du problème. La sélectivité de la membrane influe sur ce qui se passe à chacun de ses côtés, c’est-à-dire sur le perméat et dans le canal d’alimentation (rétentat). D’un point de vue fondamental, le passage de soluté dans le perméat, problème auquel on semble s’intéresser moins fréquemment, a une forte influence. En effet, il contribue à intensifier la polarisation de concentration sans forcément réduire pour autant le flux de perméat résultant. Aussi, pour des conditions opératoires données, la sélectivité membranaire modifie des comportements généralement admis comme asymptotiques mais qu’en réalité ne le sont pas. Par exemple, le taux de rétention passe par un maximum avant de décroître sous l’effet de l’augmentation de la pression d’opération.
L’importance de la perméabilité au soluté est comparable à la difficulté qu’il existe pour la déterminer de manière fiable. Cela est dû principalement à deux grandes raisons: à sa dépendance aux conditions opératoires auxquelles elle est soumise, notamment à la pression et à la concentration, et à la difficulté de quantifier ces conditions pour toute opération, notamment la concentration à laquelle la membrane est effectivement exposée quand elle est sous pression, cela du fait de la polarisation de concentration. Nos résultats ont permis de vérifier et de quantifier ces effets. Les valeurs de perméabilité au chlorure de sodium déterminées par osmose-diffusion étaient du même ordre de grandeur que celles trouvées sous pression, mais il n’y a pas eu d’accord précis et les écarts sont significatifs sur les résultats du procédé (concentration du perméat). Quant aux perméabilités à l’eau calculées dans les deux conditions, des différences de jusqu’à deux ordres de grandeur ont été trouvées. Cela indiquerait que les mécanismes de transfert membranaire entraînés par la pression ou par le gradient osmotique quand ces forces motrices sont appliquées de forme isolée ne sont pas les mêmes. Ceci nous amène à penser à, au moins, une contribution convective générée par la pression, observation qui s’oppose aux considérations du traditionnel modèle de solubilisation-diffusion.

Les limitations que nous avons constatées en relation à notre modélisation et à nos expériences fournissent des pistes de travail futur en plus d’autres perspectives que nous souhaitons approfondir:

- Considérer la variation spatiale des propriétés de la solution résultante des dépendances du coefficient de diffusion et de la viscosité avec la concentration;
- Évaluer les prédictions numériques quand d’autres modèles de transport transmembranaire sont utilisés (e.g. Kedem-Katchalsky), en cours dans notre équipe;
- Rajouter au modèle présent le phénomène de colmatage surfacique réversible, en cours dans notre équipe;
- Poursuivre le développement des codes adaptés à la géométrie cylindrique, en cours dans notre équipe;
- Étendre le modèle à trois dimensions spatiales afin de considérer des effets de paroi, potentiellement importants selon les dimensions des modules membranaires;
- Valider le modèle expérimentalement avec d’autres sels, en cours dans notre équipe.
SYNTHÈSE DES TRAVAUX

equipe;

- Valider le modèle expérimentalement dans un module plan de grandes dimensions et sans espaceur dans son canal d’alimentation, géométrie par excellence de notre approche, moins influencée par des effets de bord et de paroi;

- Étendre le modèle aux séparations de solutions contenant plusieurs solutés;

- Réaliser plus d’essais d’osmose-diffusion, avec des membranes conditionnées à des pressions transmembranaires bien différentes, à des concentrations couvrant une plage de valeurs plus vaste et avec des échantillons de plus grande surface (valeurs plus homogènes en moyenne);

- Implémenter dans les cellules de diffusion un contrôle de température et un système de mesure continue et non-destructive des hauteurs et concentrations. Aussi, réduire l’aire transversale des compartiments, afin d’observer des variations de hauteur de colonne de liquide plus grandes tout en les maintenant négligeables par rapport aux différences de pression osmotique;

- Modéliser les expériences d’osmose et diffusion avec d’autres modèles de transport et en déterminer les coefficients. Cela obligera cependant à complexifier, voire à diversifier les types et nombres d’expériences du fait de l’ajout de plus d’inconnues.