



Universidade do Porto
Faculdade de Engenharia
FEUP

New Separation Hybrid Membrane Cells - - a CFD study

by
Sónia Isabel Silva Pinto

Graduated in Chemical Engineering
by the Faculty of Engineering - University of Porto

**Dissertation presented for the degree of Doctor of Philosophy
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Centro de Estudos de Fenómenos de Transporte
Departamento de Engenharia Química
Faculdade de Engenharia da Universidade do Porto
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Supervised by
João Bernardo Lares Moreira de Campos, PhD
João Mário Rodrigues Miranda, PhD

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*Life has no sense without Dreams.
PhD was always one of them. . .*

Sónia Pinto

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To my parents . . .

To my sister . . .

To all my family . . .

To all my friends . . .

Abstract

Hybrid Membrane Cell (HMC) is a new type of membrane cell that was conceptualised in the research group “Centro de Estudios de Fenómenos de Transporte”. The starting point was the separation of one solute from its solvent through a hybrid membrane cell – cell with two types of membranes, with different porosities, alternating in juxtaposition, along the cell; semi-permeable membranes (only permeable to the solvent) and fully permeable membranes (permeable to the solutes and to the solvent). Due to the specific configuration of the hybrid cell, it was observed a reduction of the concentration polarization phenomena and an increase of the separation.

The present thesis has the main objective to explore the potential of the New Hybrid Membrane Cells, by Computational Fluid Dynamics (CFD), to separate different components in solution. Three types of HMC were explored: HMC combined with differential diffusion of the components, selective HMC and HMC with electric interactions membrane-components.

Firstly, the potential of a HMC combined with differential diffusion of two macromolecules was studied. This type of HMC is composed by several membrane sections where each one has a semi-permeable membrane (only permeable to the solvent) and a fully permeable membrane (permeable to the solutes and to the solvent), alternating along the cell. The feed stream is separated into three streams: a retentate stream, a solvent stream, which crosses the semi-permeable membranes, and a concentrate stream which crosses the fully permeable membranes. The purity and recovery of the solute with lower diffusivity in the fully permeable sub-sections (concentrated stream) show the potential of this new fractionation process. The purity increases with the solvent stream velocity, decreases with the concentrate stream velocity and increases with the number of sections. The recovery increases with the solvent stream velocity and also with the concentrate stream velocity. Moreover, the effect of the concentration on the physical properties was studied for this new fractionation process. The variation of the transport properties, for high levels of concentration polarization, influences the separation since the purity of the less diffusive component increases in the concentrate stream. This increase can reach 20%.

Afterwards, the potential of the selective Hybrid Membrane Cell was explored by CFD. This type of HMC is composed by several membrane sections in series. Each membrane section has a semi-permeable sub-section selective to the solutes and permeable to the

solvent and a fully-permeable sub-section totally permeable to the solutes and to the solvent. The apparent selectivity of the separation of two macromolecules was determined. The results show that the fully permeable membranes contribute to the cleaning of the mass boundary layer over the semi-permeable membranes, reducing concentration polarization and transmission of the components. Consequently, for a range of high transmembrane pressure, where a conventional cell polarizes, the apparent selectivity through the semi-permeable membranes increases, when a HMC is used. This selectivity increases for increasing velocity of the concentrate stream and number of sections.

The potential of Hybrid Membrane Cells with electric interactions membrane-components was also analyzed by numerical studies. A numerical code was developed to solve, simultaneously, the Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations. The HMC studied is composed by several membrane sections, where each section has a semi-permeable sub-section (permeable to the solvent and impermeable to the solutes) electrically charged and a fully permeable sub-section (permeable to the solvent and to the solutes) electrically neutral. The numerical results were compared with those obtained in a neutral hybrid membrane cell. By selecting semi-permeable membranes with the same charge of the macromolecules with higher diffusivity, these macromolecules move away further from the membrane, while those with lower diffusivity approach, further, the membrane. However, due to interactions between the electric and concentration fields in the region crossed by the streamlines of the concentrate stream, the separation in the fully permeable membrane is reduced.

In a conventional cell, with only one semi-permeable membrane selective to the solutes, electric interactions between membrane and solutes increase the efficiency of the separation. The most transmitted component through the membrane pores (lower rejection) is the component with opposite electric charge to the charge of the membrane. The apparent selectivity considering an electrically charged membrane is, in the studied case, 17% higher than the apparent selectivity in a neutral membrane. The potential of a selective Hybrid Membrane Cell with electric interactions membrane-components is still in study.

Keywords: hybrid membrane cell, separation processes, computational fluid dynamics, separation by differential diffusivity, macromolecules fractionation, separation by electric interactions membrane – solutes.

Resumo

Célula de Membrana Híbrida (HMC) é um novo tipo de célula que foi conceptualizado no grupo de investigação “Centro de Estudos de Fenómenos de Transporte”. O ponto de partida foi estudar a separação de um soluto do seu solvente através de uma célula de membrana híbrida – célula com dois tipos de membranas de diferentes porosidades, alternadas em justaposição ao longo da célula; membrana semi-permeável (apenas permeável ao solvente) e membrana totalmente permeável (permeável ao soluto e ao solvente). Devido à configuração específica da célula híbrida, foi observada uma redução do fenómeno da polarização da concentração e um aumento da separação.

A tese presente tem como principal objectivo explorar o potencial destas Células de Membranas Híbridas, através da Dinâmica de Fluidos Computacional (CFD), para separar diferentes componentes em solução. Três tipos de HMC foram explorados: HMC combinada com diferença de difusividade dos componentes, HMC selectiva aos componentes e HMC com interacções eléctricas membrana – componentes.

Em primeiro lugar, foi estudado o potencial da HMC combinada com diferença de difusividade de duas macromoléculas. Este tipo de HMC é composto por várias secções de membranas, cada uma com uma membrana semi-permeável (apenas permeável ao solvente) justaposta a outra totalmente permeável (permeável aos solutos e ao solvente). A corrente de entrada é, então, separada em três correntes: uma corrente de retido, uma corrente de solvente que atravessa as membranas semi-permeáveis e uma corrente de concentrado que atravessa as membranas totalmente permeáveis. A pureza e a recuperação do soluto, com mais baixa difusividade, nas sub-secções totalmente permeáveis (corrente de concentrado) mostram o potencial deste novo processo de fraccionamento. A pureza aumenta com a velocidade da corrente de solvente, diminui com a velocidade da corrente de concentrado e aumenta com o número de secções. A recuperação aumenta com a velocidade da corrente de solvente e também com a velocidade da corrente de concentrado. Para além disso, o efeito da concentração nas propriedades físicas dos componentes foi estudado para este novo processo de fraccionamento. A variação das propriedades de transporte, para elevados níveis de polarização da concentração, influencia a separação, uma vez que a pureza do componente menos difusivo aumenta na corrente de concentrado, aumento este que pode atingir os 20%.

De seguida, o potencial da HMC selectiva aos componentes foi explorado através de CFD. Este tipo de HMC é composto por várias secções em série. Cada secção tem uma sub-

secção com uma membrana semi-permeável, selectiva aos solutos e permeável ao solvente, e uma sub-secção com uma membrana totalmente permeável aos solutos e ao solvente. A selectividade aparente da separação de duas macromoléculas foi determinada. Os resultados mostram que as membranas totalmente permeáveis contribuem para o efeito de limpeza da camada limite de massa à superfície das membranas semi-permeáveis, reduzindo a polarização da concentração e a transmissão dos componentes. Consequentemente, para uma gama de pressões transmembranares elevada, onde uma célula convencional polariza, a selectividade aparente, quando se utiliza uma HMC, através das membranas semi-permeáveis aumenta. Esta selectividade é tanto maior quanto maior é a velocidade da corrente de concentrado e o número de secções.

O potencial da HMC com interacções eléctricas membrana – componentes foi também analisado através de estudos numéricos. Um código numérico foi desenvolvido para resolver, simultaneamente, as equações de Poisson-Boltzmann, Nernst-Planck e Navier-Stokes. A HMC estudada é composta por várias secções de membranas, onde cada secção tem uma sub-secção semi-permeável (permeável ao solvente e impermeável aos solutos) carregada electricamente e uma sub-secção totalmente permeável (permeável ao solvente e aos solutos) electricamente neutra. Os resultados numéricos foram comparados com os obtidos através de uma célula de membrana híbrida electricamente neutra. Seleccionando membranas semi-permeáveis com a mesma carga das macromoléculas de maior difusividade, estas macromoléculas afastam-se muito da membrana, enquanto as de menor difusividade se aproximam consideravelmente. Contudo, devido às interacções entre os campos eléctricos e de concentração na região atravessada pelas linhas de corrente de concentrado, a separação nas membranas totalmente permeáveis diminui.

Numa célula convencional, com apenas uma membrana semi-permeável selectiva aos solutos, as interacções eléctricas entre a membrana e os solutos aumentam a eficiência da separação. O componente com maior transmissão através da membrana (menor rejeição) tem de ter carga eléctrica oposta à da membrana. A selectividade aparente considerando uma membrana carregada electricamente é, neste caso estudado, 17% mais elevada do que a selectividade aparente numa membrana neutra. O potencial da HMC selectiva aos componentes e com interacções eléctricas membrana – componentes encontra-se ainda em desenvolvimento.

Palavras-chave: célula de membrana híbrida, processos de separação, dinâmica de fluidos computacional, separação por diferença de difusividade, fraccionamento de macromoléculas, separação por interacções eléctricas membrana – solutos.

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Chapter 1

General Introduction

Supported in a generic bibliography revision, this chapter describes the motivation and relevance of the New Hybrid Membrane Cells under study for the membrane separation processes. The main objectives and the outline of the thesis are also presented.

1.1. Motivation

The Hybrid Membrane Cell (HMC) is a new concept of cell incorporating an innovative type of hybrid membrane to perform separations. This new concept “was born” in the research group I belong (Centro de Estudios de Fenómenos de Transporte - CEFT). The starting point was the study concerning the separation of a solute from its solvent [1]. According to this study, the separation in a HMC can be much more efficient than in a Conventional Cell (CC). The explanation is the reduction of the concentration polarization phenomena due to the configuration of the hybrid membrane, the so-called cleaning boundary layer effect.

The challenge, I was facing, was the exploitation of the potential of this new concept of cell to fractionate macromolecules, process with growing interest in the industry. Three different separations, based on different mechanisms in a HMC, are explored sequentially in this thesis. Firstly, it is explored the potential of a HMC to perform the separation of two macromolecules by differential diffusion. In a second step, it is explored the potential of a selective HMC (different transmissions of macromolecules through the hybrid membrane). At last, it is explored the potential of the electric interactions between the hybrid membrane and the macromolecules to increase the purity and selectivity of the separation in a HMC.

A numerical code based on Computational Fluid Dynamics has been successively developed and implemented to perform the study.

1.2. Bibliography revision

This bibliography revision has the main objective of introducing concepts for a better understanding of the following chapters of the thesis. Those chapters, based on published or submitted scientific papers, have, each one, a detailed bibliography revision according to the topic under study.

1.2.1. Membrane separation processes

In the last years, there has been a growing interest in the developing of membrane separation processes. These processes offer several advantages and so they are replacing the traditional centrifugation, distillation and extraction processes. Among the advantages,

energy efficiency should be highlighted, since there is no phase change, and also those inherent to a continuous and modular process.

In the industry, the membrane separation processes have been applied in several fields such as food industry and biotechnology, pharmaceutical and medical industry, purification of water and water treatment, textile and petrochemical industries and nuclear power plants [2-8]. Table 1.1 shows the main applications in each field.

Table 1.1 – Some applications of membrane separation processes.

Field	Application
Food Industry	- separation of milk proteins
	- concentration of fruits for juice
	- concentration of grapes for wine
	- concentration of liquids with sugar
	- recuperation and concentration of proteins and amino-acids
	- lactose recuperation from cheese serum
	- treatment of soy serum
	- treatment of residues from alcohol distillation
Pharmaceutical and Medical Industry	- concentration of medical herbs - ultrapure water production
Water treatment	- removal of volatile organic compounds from wastewater
	- treatment and removal of nitrogen and phosphorus from residual water
Water production	- desalination of seawater
	- desalination for industrial application
	- desalination for ultrapure water production
Textil Industry	- treatment and recuperation of inks and oils from water
Petrochemical Industry	- residues water treatment contaminated with oil derivatives
Nuclear	- radioactive water treatment from drainage

The role of the membrane in the separation process is to act as a thin, permeable and selective barrier. When a driving force is applied, the membrane allows the transfer of single or multiple components between two regions which are physically separated. This driving force can induce one or more of the following gradients through the membrane:

- pressure gradient (microfiltration, ultrafiltration, nanofiltration, reverse osmosis and gas permeation);
- concentration gradient (dialysis and haemodialysis);
- combining pressure and concentration gradients (pervaporation);
- electric potential gradient (electric dialysis and electrolysis);
- temperature gradient (thermal-osmosis).

Microfiltration, ultrafiltration and nanofiltration are processes in which the membrane retains large molecules and allows the passage of smaller ones through the application of a pressure driving force between the two sides of the membrane. The difference between these processes is the size of the membrane pores, retaining molecules of different size [9], as it can be seen in Table 1.2.

Table 1.2 – Membrane processes based on pressure gradients.

Membrane process	Type of species to separate	Size of species
Microfiltration	bacteria, flour, coal dust	0.1 - 10 μm
Ultrafiltration	virus and proteins	0.01 - 0.1 μm
Nanofiltration	mineral salts	0.001 - 0.01 μm
Reverse Osmosis	ions and salts with low molecular weight	$< 0.001 \mu\text{m}$

Reverse osmosis is quite similar to microfiltration, ultrafiltration and nanofiltration processes. The main differences are, not only in the particle size, but also in the type of membrane used. The membrane used for a reverse osmosis process has a dense and homogeneous layer. In reverse osmosis, the osmotic pressure (exercised force to the passage of the solute/solvent) of the solution is high, due to the very small size of the particles, and so the hydrostatic pressure gradient through the membrane must be also high to overlap the osmotic pressure gradient. Reverse osmosis and nanofiltration are both used in the desalination of seawater. Furthermore, reverse osmosis is used in the recuperation of wastewater from industry services and in the water purification for human consumption.

In the pervaporation separation process, the component (solute) of a liquid solution is preferably transferred to the other side of the membrane in the state of vapour, i.e., a liquid/vapour separation process where the solute is partially vaporised through the dense

membrane. Pervaporation and reverse osmosis processes are frequently used together in the separation of volatile organic compounds from wastewater [10].

In the dialysis separation process, the solute with different concentrations on each side is separated through the semi-permeable membrane. The mass transfer is from the region of higher concentration to that of lower concentration. The mass flux depends on the molecular weight of the species (usually around the nanometre order) and also on the characteristics of the membrane.

In the electric dialysis separation process, ions or salts (nanometer sized species) with low molecular weight are transferred through the membrane due to an applied electric potential. The operational conditions are similar to those used for reverse osmosis.

The ultrafiltration membrane processes are used in this study to fractionate macromolecules. The separation of macromolecules can be done not only by the difference between the size of the macromolecules and the pores, but also by taking advantage of the difference between the molecular diffusivity of the components.

There are several separation processes taking advantage of this diffusivity difference, namely: diffusion separation [11], thermal diffusion separation [12], Brownian motors [13], field-flow fractionation (FFF) [14,15], flow field-flow fractionation (FlFFF) [16,17] and split flow-thin cell (SPLITT) fractionation [18,19]. FlFFF and SPLITT processes have importance for the development of this work, reason why they are going to be described in more detail.

The flow field-flow fractionation process (FlFFF) is performed in a parallel plate cell with two feed streams: the channel flow and the crossflow (Figure 1.1). The channel flow is along the horizontal direction and the crossflow along the vertical one. The upper plate is fully-permeable (permeable to the solute and to the solvent) and the lower plate is only permeable to the solvent. The accumulated solute in the lower plate leaves the membrane surface by diffusion and is dragged by the channel flow. By consequence, the outflow stream, the one that leaves the channel, is rich in solute and the outflow stream, the one that crosses the membrane, is rich in solvent (Figure 1.1).

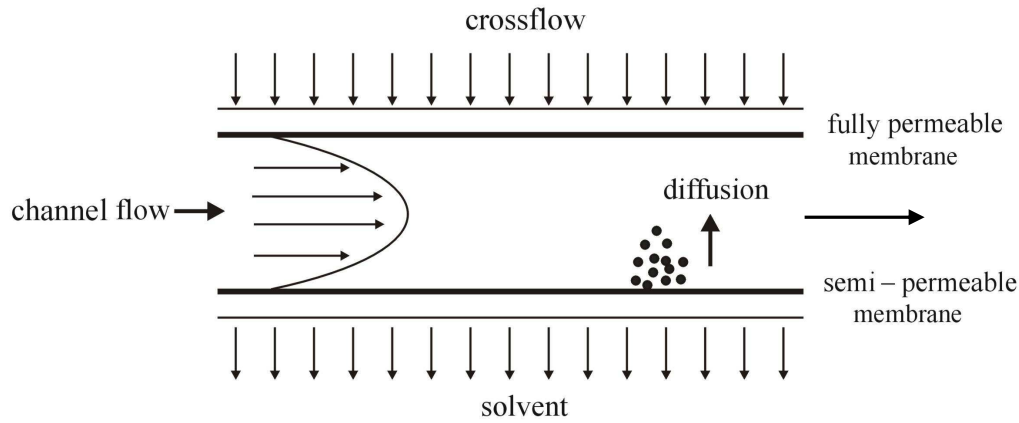


Figure 1.1 - Schematic representation of FIFFF process in a parallel plate cell.

In the split flow-thin cell process (SPLITT), the feed solution with two solutes is divided by a splitter into two outflow streams with different compositions. This division is done according to the diffusivity of the solutes (Figure 1.2).

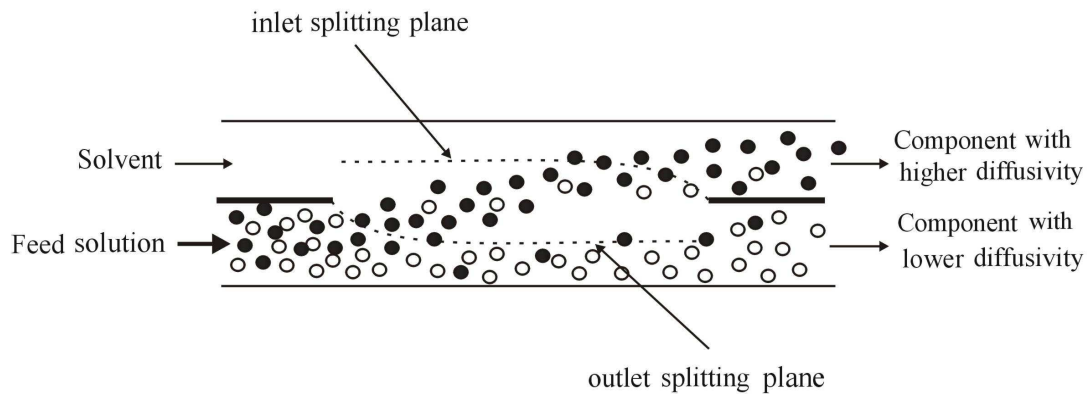


Figure 1.2 - Schematic representation of SPLITT process in a parallel plate cell.

1.2.2. Concentration polarization phenomena in a pressure driven process

The simplest membrane cell (Figure 1.3) is basically composed by two compartments: the retentate and the permeate compartments, which are separated by the semi-permeable membrane. The membrane is, most of the times, partially permeable to the solute and fully permeable to the solvent. There are also an inlet stream (a feed stream) and two outlet streams: the concentrate stream (in the retentate side) and the permeate stream (in the permeate side). The concentrate stream is rich in the solute and the permeate stream in the solvent.

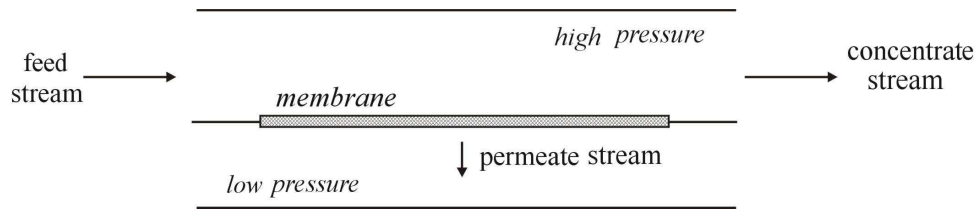


Figure 1.3 – Schematic representation of a membrane separation cell.

Due to the pressure gradient and to the molecules dimensions, the solvent passes to the other side of the membrane, while the solute accumulates partially at the membrane surface. This accumulation induces the build-up of a mass boundary layer over the membrane. At the same time, due to the gradient concentration in the boundary layer, the solute diffuses into the bulk direction. In steady state, the solute transported by convection into the perpendicular direction to the membrane plus the solute transported through the membrane is equal to the solute transported by diffusion into the bulk (opposite direction). The result is a layer with high solute concentration, which reduces the permeate velocity (Figure 1.4). The permeate velocity decreases due to the increase of the osmotic pressure difference through the membrane, induced by the high solute concentration layer over the membrane. This phenomenon is called the concentration polarization of the membrane.

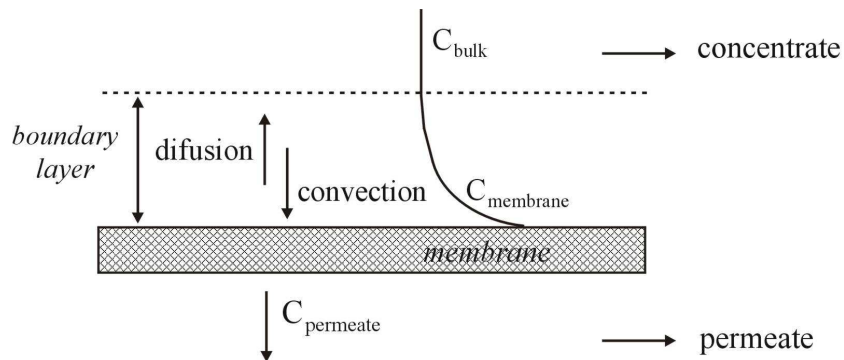


Figure 1.4 – Concentration polarization phenomenon.

1.2.2.1. Film equation based on a convective-diffusive model in a pressure driven separation process

The stagnant film theory gives a simplified equation to describe the solute transport in the vicinity of the membrane.

The assumptions of the stagnant film theory are:

- solvent and solute with similar densities;
- constant diffusion coefficient;
- negligible tangential, to the membrane, concentration gradients, comparatively to the normal gradients;
- semi-stagnant fluid film of thickness, δ , in the membrane adjacent layer, where the tangential component of the velocity is null and the normal component is different from zero;
- perfectly mixed fluid far from the semi-stagnant film, and consequently uniform concentration;
- the permeate flux crossing the semi-stagnant film does not vary with the distance to the membrane;

A solute mass balance in steady state can be performed in the vicinity of the membrane:

$$V_m C = -D \frac{\partial C}{\partial Z} + V_m C_p \quad (1.1)$$

where V_m is the permeate velocity, C and C_p are, respectively, the solute concentration at a distance Z from the membrane and in the permeate flux, while D is the molecular diffusivity of the solute in the solvent.

The result of the integration of equation (1.1), with the appropriate boundary conditions, is:

$$V_m = -\frac{D}{\delta} \ln \left(\frac{C_m - C_p}{C_0 - C_p} \right) \quad (1.2)$$

where C_m and C_0 are, respectively, the solute concentration of a component at the membrane surface and in the bulk and δ is the thickness of the boundary layer. This equation is usually called the *Stagnant Film Equation* [20] originally developed by Brian [21].

The ratio between the solute diffusivity (D) and the stagnant film thickness (δ) is set equal to the solute mass transfer coefficient, k :

$$k = \frac{D}{\delta} \quad (1.3)$$

The application of the film equation has always the problem concerning the quantification of k , since δ is a parameter of the model.

To solve this problem, a mass transfer coefficient from an impermeable system is generally adopted and the stagnant film equation becomes:

$$V_m = -k^I \ln \left(\frac{C_m - C_p}{C_0 - C_p} \right) \quad (1.4)$$

where the superscript I refers to impermeable systems.

Empirical correlations are frequently used to obtain k^I , either correlations from mass transfer data in impermeable soluble systems with uniform surface concentration (Figure 1.5a), as correlations from mass transfer data in impermeable soluble systems with uniform mass flux at the wall (Figure 1.5b).

The use of the film equation with mass transfer coefficient data from impermeable systems has been theme of discussion in the literature [22-24]. Zydney [24] provided a fundamental understanding of the mathematical basis for the stagnant film formalism and a quantitative description of the limitations of the model for a parallel plate cell.

To clarify the limitations of the film equation, Miranda and Campos (2002) [20] studied numerically, by solving the conservative equations, the concentration and velocity profiles in both, permeable and impermeable systems. The flow and the mass transport equations were solved simultaneously, since the solute concentration in a permeable cell depends on the permeate velocity.

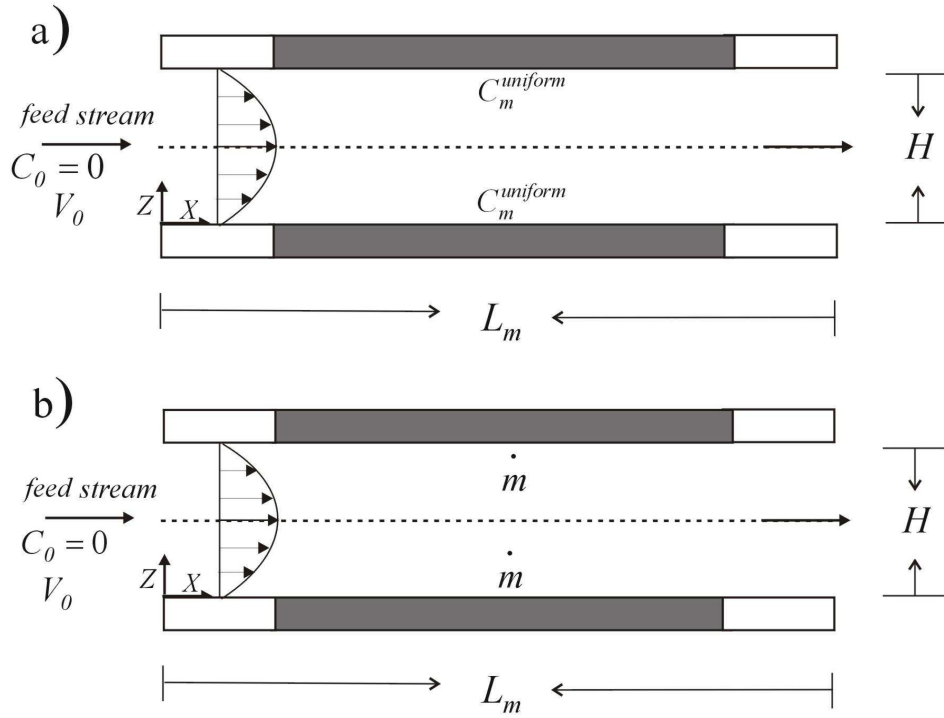


Figure 1.5 – Sketch of a) impermeable parallel plate cell device with uniform solute concentration at the wall; b) impermeable parallel plate device with uniform mass flux at the wall.

Supposing total rejection of the solute [20], equation (1.4) can be rewritten as:

$$\frac{V_m}{V_0} = -\frac{\text{Sh}^I}{\text{Pe}} \ln\left(\frac{C_m}{C_0}\right) \quad (1.5)$$

where Sh^I is the Sherwood number for an impermeable parallel plate cell:

$$\text{Sh}^I = \frac{k^I H}{D} \quad (1.6)$$

and Pe is the Peclet number:

$$\text{Pe} = \frac{V_0 H}{D} \quad (1.7)$$

where V_0 is the inlet velocity and H the height of the cell.

For predefined operation conditions, permeate velocity and membrane surface concentration predictions were used to calculate Sh^I (equation 1.5). These Sh^I values were compared with those numerically obtained in an identical impermeable system with uniform mass flux at the wall (Figure 1.5b) or uniform concentration at the wall (Figure 1.5a). From this comparison, the strengths and limitations of the film equation were identified by Miranda and Campos (2002) [20]. The accuracy of the film equation decreases by increasing the inlet velocity, V_0 , and decreasing the diffusivity of the solute component and the viscosity of the solution.

1.2.2.2. Carman-Kozeny equation applied to pressure driven separations

In a pressure driven separation process, the effective pressure (P_{eff}) is:

$$P_{eff} = P - \pi \quad (1.8)$$

where P is the static pressure and π the osmotic pressure.

The effective pressure difference (ΔP_{eff}), between both sides (concentrate and permeate sides) of the membrane is then given by:

$$\Delta P_{eff} = \Delta P - \Delta \pi \quad (1.9)$$

where $\Delta \pi$ is the osmotic pressure difference between the retentate over the membrane (π^m) and the permeate (π^p), and ΔP is the static pressure difference across the membrane.

The osmotic pressure of a solution depends on the solute concentration: it is zero when there is no solute and increases when the solute concentration increases. The osmotic pressure is lower than the hydrostatic pressure. Therefore, the higher is the osmotic pressure over the membrane (π^m), the lower is the effective pressure driven force.

The permeate velocity, V_m , is determined by the ratio between the effective driven force (ΔP_{eff}) and the flow resistance ($R_m \mu$), following Carman-Kozeny equation [25]:

$$V_m = \frac{\Delta P_{eff}}{R_m \mu} = \frac{\Delta P - \Delta \pi}{R_m \mu} \quad (1.10)$$

The flow resistance depends on the viscosity of the permeate flux (μ) and on the membrane resistance (R_m) which depends on its structural characteristics: geometry, dimensions, number and size of pores and their distribution.

According to the previous equation, the osmotic pressure, resulting from the accumulation of the solute over the membrane (Figure 1.4), has a direct effect on the permeate velocity, i.e., increasing the osmotic pressure difference (solute concentration) decreases the velocity. This phenomenon is schematically represented in Figure 1.6, for a parallel plate cell.

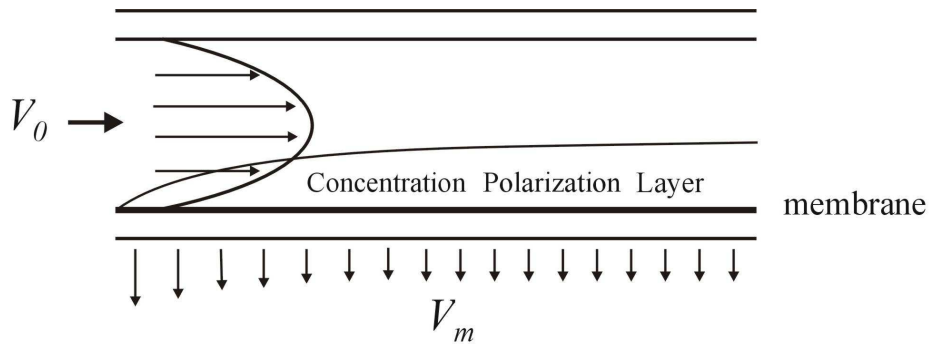


Figure 1.6 - Schematic representation of an ultrafiltration process in a parallel plate cell.

1.2.2.3. Non-dimensional groups of a pressure driven separation

The importance of the osmotic pressure difference of a component in the permeate velocity is measured by the following non-dimensional number:

$$\Pi_{\Delta \pi_0} = \frac{\Delta \pi_0}{\Delta P} = \frac{\pi_0^m - \pi^P}{\Delta P} \quad (1.11)$$

where the subscript o refers to the inlet conditions and π_0^m is the osmotic pressure over a non-polarized membrane (inlet concentration, C_0 , at the membrane surface).

Beyond this, if the solute is completely rejected ($\pi^p = 0$), the previous non-dimensional group is re-written, respectively, as:

$$\Pi_{\pi_0} = \frac{\pi_0^m}{\Delta P} \quad (1.12)$$

Furthermore, the non-dimensional group

$$\Pi_v^0 = \frac{\Delta P - \Delta \pi_0}{R_m \mu V_0} \quad (1.13)$$

represents the ratio between the permeate velocity at inlet conditions, defined by Carman-Kozeny equation, equation (1.10), and the average velocity at the cell inlet (V_0), i. e., the normalized permeate velocity at inlet conditions.

1.2.2.4. Selectivity in a binary pressure driven separation

The decrease of the permeate velocity is not the only effect of the concentration polarization phenomenon. As long as the solute concentration in the vicinity of a membrane increases, the probability of a particle of solute to cross the membrane also increases. For this reason, the concentration polarization is also responsible for a lower selectivity of a given separation. Therefore, it is necessary to control the concentration polarization to control the membrane selectivity.

Selectivity (σ) in a binary separation is defined by the ratio between the transmission of the preferentially transmitted component (S_1) and the transmission of the preferentially retained component (S_2) [26]:

$$\sigma = \frac{S_1}{S_2} \quad (1.14)$$

The transmission of solutes (S_i) across the membrane was analyzed and described, through a convective-diffusive transport model, by Opong and Zydney [27]. These authors

used three distinct theoretical approaches to describe the transport in porous membranes: the Kedem-Katchalsky analysis [28, 29]; the Stefan-Maxwell multicomponent diffusion equations [30, 31]; and hydrodynamic models [32, 33]. The first two approaches are developed directly from irreversible thermodynamics principles; they both lead to a set of phenomenological equations relating the solute and solvent fluxes to pressure and concentration gradients. On the other hand, the hydrodynamic models evaluate the solute flux by directly solving the governing hydrodynamic equations for the motion of a single solute in a well-defined pore. From these equations, the transport parameters were expressed in terms of solute (supposing spherical particles) and pore characteristics (axisymmetric pores).

1.2.2.5. Concentration polarization phenomena investigated in previous works by my research group

In the latest years, the concentration polarization phenomena have been investigated in my research group (Centro de Estudos de Fenómenos de Transporte). Mass transport in pressure driven membrane cells, impinging jet cell [34] and parallel plate cell (Figure 1.6), has been studied. Computational Fluid Dynamics (CFD) packages were developed to simulate the flow and mass transport in these membrane cells and a new CFD technique was developed to deal with large permeate velocities and very thin boundary layers [35]. The accuracy of the classical film equation was evaluated [20] and mass transport regimes were identified [20, 34, 36, 37].

Variable physical properties as molecular diffusivity, fluid viscosity and osmotic pressure of the solution must be taken in account in the study of the polarization phenomena. A high viscous solution at the membrane surface induces a decrease in the tangential velocity, with direct effect on the concentration polarization. Moreover, a solution with low diffusivity at the membrane surface contributes to the build up of a very concentrate layer with, also, direct effect on the concentration polarization. Afonso, Miranda and Campos [38] studied numerically the variation of the physical properties with solute concentration at the vicinity of a membrane surface, in order to describe the effects of this variation on the polarization phenomena.

1.2.3. Macromolecule fractionation by ultrafiltration

There has been an increasing interest in the development of membrane ultrafiltration processes for the fractionation of macromolecules, particularly for protein mixtures. When compared with the widely used electrophoresis and chromatographic separation processes, ultrafiltration exhibits the advantages of a high throughput and an easy scale-up. The potential for achieving high-resolution protein fractionation using ultrafiltration has been demonstrated in the literature [39]. The selectivity of macromolecules fractionation by ultrafiltration depends on the operating conditions such as transmembrane pressure and cross-flow velocity; physicochemical conditions such as pH, salt concentration and feed concentration; and resultant conditions such as the extent of concentration polarization and fouling [26, 40].

1.2.4. Hybrid membrane systems and Hybrid membrane cells

The main objective of the present work is to study, by numerical methods, the fractionation of macromolecules by ultrafiltration in a new concept of cell: a Hybrid Membrane Cell (HMC).

The hybrid membrane cell (HMC), explored in this thesis, and hybrid membrane systems (HMS), take advantages in the efficiency of membrane separation processes. These advantages are going to be explained. Figure 1.7 and Figure 1.8 represent examples of HMC and HMS, respectively.

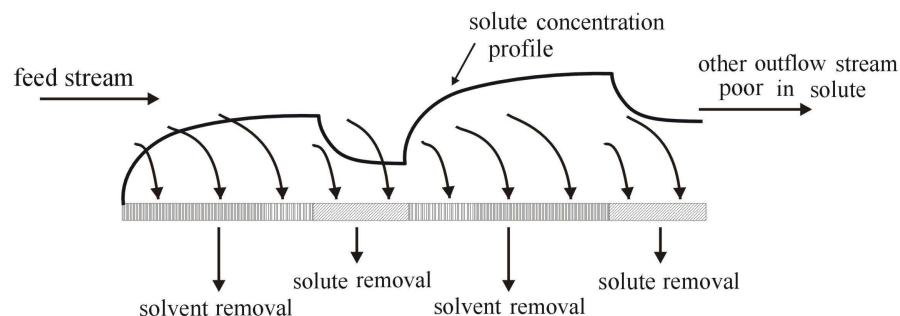


Figure 1.7 - Example of a Hybrid Membrane Cell (HMC).

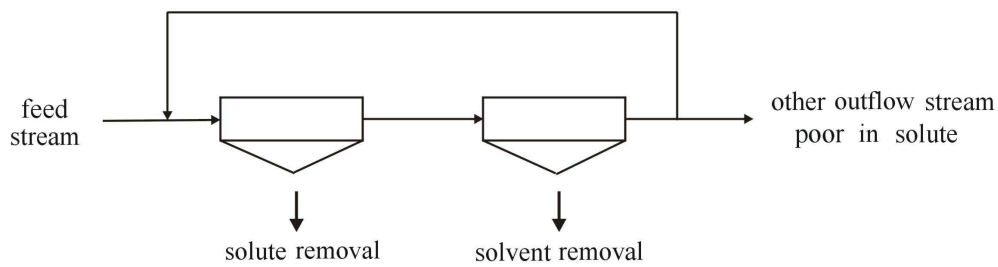


Figure 1.8 - Example of a Hybrid Membrane System (HMS).

Hybrid membrane systems combine two unit operations. Generally, one unit operation is a solvent removal operation and the other is a solute removal operation (Figure 1.8). The hybrid membrane cells are separation cells that combine different membranes in series. Usually, one of the membranes is a solvent removal membrane and the other a solute removal membrane (Figure 1.7).

Hybrid membrane systems have been subject of investigation by Ray et al. [10]. The authors showed that the combination of solvent removal and solute removal operations improves the efficiency of individual operations. One of their case studies is the combination of a pervaporation module with a reverse osmosis module [10]. The pervaporation module is the solute removal and the reverse osmosis module the solvent removal (Figure 1.8).

A HMS does not solve the concentration polarization problem in each module. To do so, it is necessary to join the membranes of both processes, just as solute removal and solvent removal, in the same module, Figure 1.7. In this module, concentration polarization will be reduced and the efficiency will be further increased.

Binning [41] propose the use of a cell with two different membranes, each one permeable to one of the components of a binary mixture. In this system, the retentate composition remained equal to the feed concentration. Shaw et al [42] demonstrated that in a reverse osmosis process, the productivity increases by introducing intermediate non-rejecting membrane sections in the cell. A similar idea was proposed by Lee and Lightfoot [43], Schubert and Todd [44] and Mitrovic and Radovanovic [45]. Lee and Lightfoot made some preliminary simulations of an ultrafiltration cell with removal of fluid from the boundary layer. They found an increased efficiency in the fractionation process studied. Schubert and

Todd proposed the recovery of fluid rich in solute from the boundary layer in several locations along the membrane. Mitrovic and Radovanovic [45] studied, by numerical methods, a cell with two different membranes in series. Nitsche and Zhuge [46] studied anti-polarization dialysis, where two membranes are used, a longitudinal dialysis membrane permeable to the solute and a transversal membrane impermeable to the solute but permeable to the solvent. The transversal membrane polarization and the longitudinal membrane polarization annihilate each other.

All these studies introduced the concept of Hybrid Membrane Cell. Miranda and Campos (2007) [1] studied the reduction of concentration polarization phenomenon when a solute is removed from its solvent, through a HMC with semi and fully permeable membrane sub-sections alternating in series (Figure 1.9).

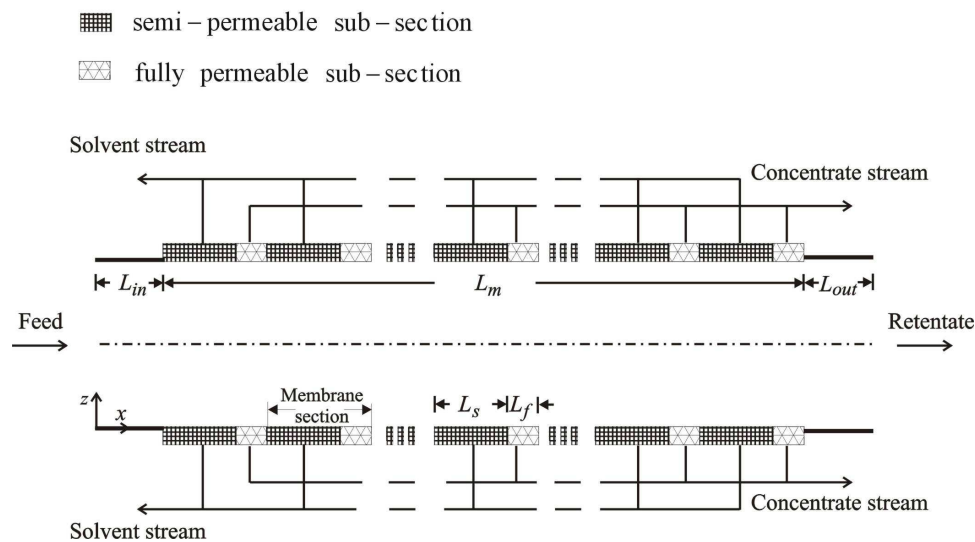


Figure 1.9 – Hybrid Membrane Cell with semi and fully permeable sub-sections to separate one solute from its solvent [1].

In this type of HMC, the boundary layer is cleaned by the fluid leaving the cell through the fully permeable membranes. This fluid follows the streamlines represented in Figure 1.10. Near the membrane surface, the fluid crosses the mass boundary layer dragging solute by convection and, afterwards, permeates the fully permeable membrane.

Since the concentrate stream cleans the mass boundary layer, the surface concentration decreases after each fully permeable membrane as is shown in Figure 1.11.

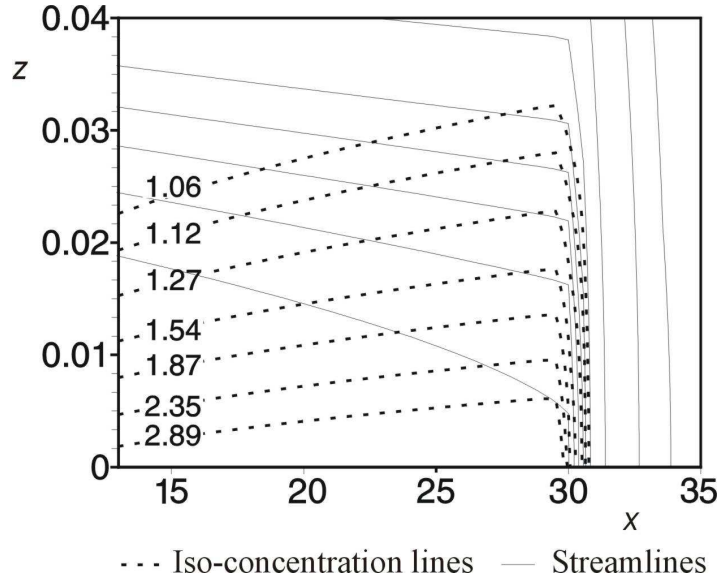


Figure 1.10 – Iso-concentration lines and streamlines along the first of four membrane sections

($\Pi_{\pi_0} = 0.1$; $\Pi_v^s = 10^{-4}$; $\Pi_v^f = 10^{-2}$; $l_m = 100$; $\varepsilon = 0.1$; $Pe = 10^6$) [1].

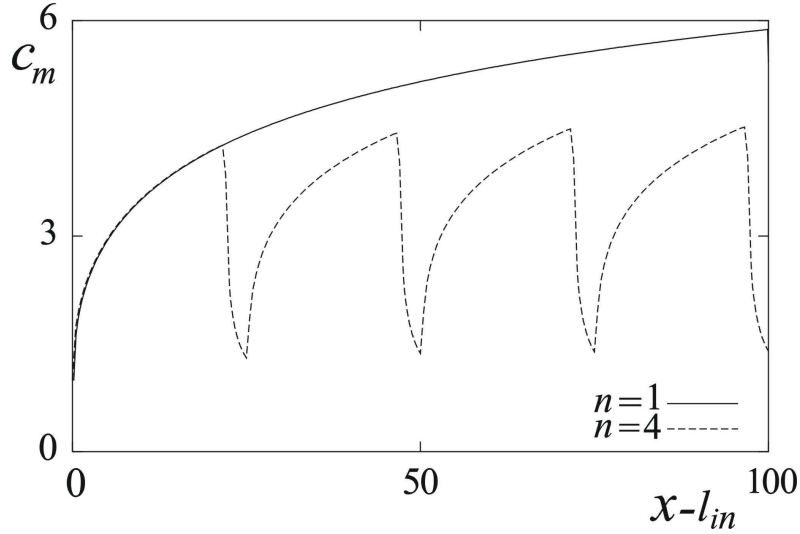


Figure 1.11 - Membrane surface concentration along a cell with four membrane sections and

comparison with a conventional cell ($\Pi_{\pi_0} = 0.1$; $\Pi_v^s = 10^{-4}$; $\Pi_v^f = 5 \times 10^{-4}$; $l_m = 100$;

$\varepsilon = 0.1$; $Pe = 10^6$) [1].

This process takes advantages of the highly concentrated fluid in the polarized boundary layer to achieve a better separation and to reduce the polarization effects on membrane efficiency. High solute recovery and low polarization levels are achieved comparatively to a conventional cell [1].

1.3. Main objectives of the thesis

As enunciated in the motivation, the main objective of this thesis is to explore the potential of different types of Hybrid Membrane Cells to perform macromolecules separation. A complex numerical code was developed in order to study the influence of several operational parameters in the purity, recovery and selectivity of the separation in a HMC. This study has relevance in food industry, more precisely for the milk proteins fractionation, and in water treatment, more concretely for the separation of volatile organic compound from wastewater, as examples.

Before describing the new three types of HMC, it is pertinent to describe, in same detail, the separation mechanisms that will used.

The separation of the components, based on diffusivity differences, has characteristics of FLFFF and SPLITT processes (above described). In these separation processes by diffusion, there is a cross-flow in the vertical direction (as FLFFF process) and separation in two outflow streams (as SPLITT process) (Figure 1.12). When the components to separate have significant differences on the molecular diffusivity and similar size and weight, the component with low diffusivity remains concentrated near the membrane and the component with higher diffusivity diffuses away from the membrane. The stream that crosses the membrane is rich in the component with low diffusivity and the outflow stream is rich in the component with high diffusivity (Figure 1.12). The concentration polarization is present due to the permeation process.

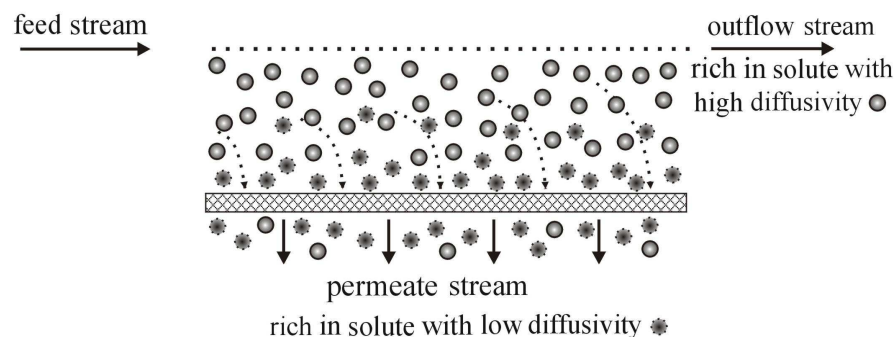


Figure 1.12 - Macromolecules fractionation by differential diffusion.

When the components to be separated have significant differences in molecular size, the macromolecules can also be fractionated by the selective membrane: the pores will reject preferentially one type of component (with higher molecular size) and transmit preferentially the other (with lower molecular size) (Figure 1.13). The differences in the diffusivity of the macromolecules can also improve, or worsen, the efficiency of the separation.

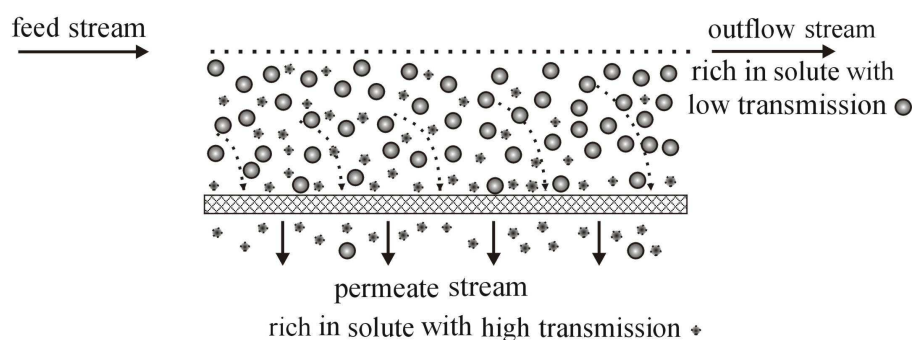


Figure 1.13 - Macromolecules fractionation by the selective membrane.

When an electrically charged membrane is used, macromolecules with opposite electric charge will be attracted to the membrane surface. Macromolecules with the same electric charge will be repelled away from the membrane surface. The efficiency of the fractionation process can further increase if the most transmitted component has opposite electric charge relatively to the electric potential of the membrane surface (Figure 1.14). The transmission of the highest transmitted component can further increase due to the increase of concentration at the membrane surface induced by electric attraction. However, if the component with the highest transmission has the same electric charge as the membrane, the electric effects will overlap, decreasing the respective transmission.

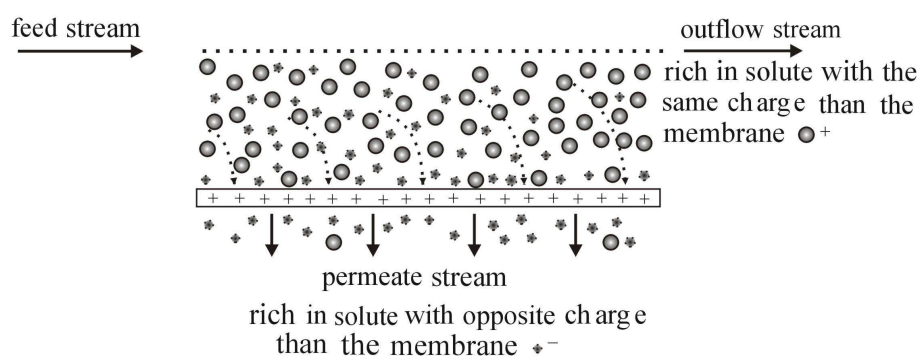


Figure 1.14 - Macromolecules fractionation by electric interaction between membrane and macromolecules.

Having in mind the mechanisms described, three new types of HMC were developed and studied by numerical methods (CFD):

A- The first type of HMC (Figure 1.15) is composed by two kinds of ultrafiltration membranes alternating in series: the semi-permeable sub-sections are impermeable to the solute and permeable to the solvent and the fully permeable sub-sections are both permeable to the solute and to the solvent. This HMC is designed to optimize the fractionation of macromolecules. In this specific case, the macromolecules separation is done by differential diffusivity. The solute with low diffusivity remains concentrated at semi-permeable surface while the solute with high diffusivity leaves from the membrane into the bulk. Then the solute with low diffusivity, accumulated at the semi-permeable surface, is recovered at the fully-permeable sub-section. The retentate stream is rich in the solute with higher diffusivity. Figure 1.15 represents this cell with two sections ($n = 2$), each one with the two sub-sections (semi and fully permeable membranes). However, the HMC was studied with much more sections, since increasing the number of sections, the concentration polarization phenomena is even more reduced.

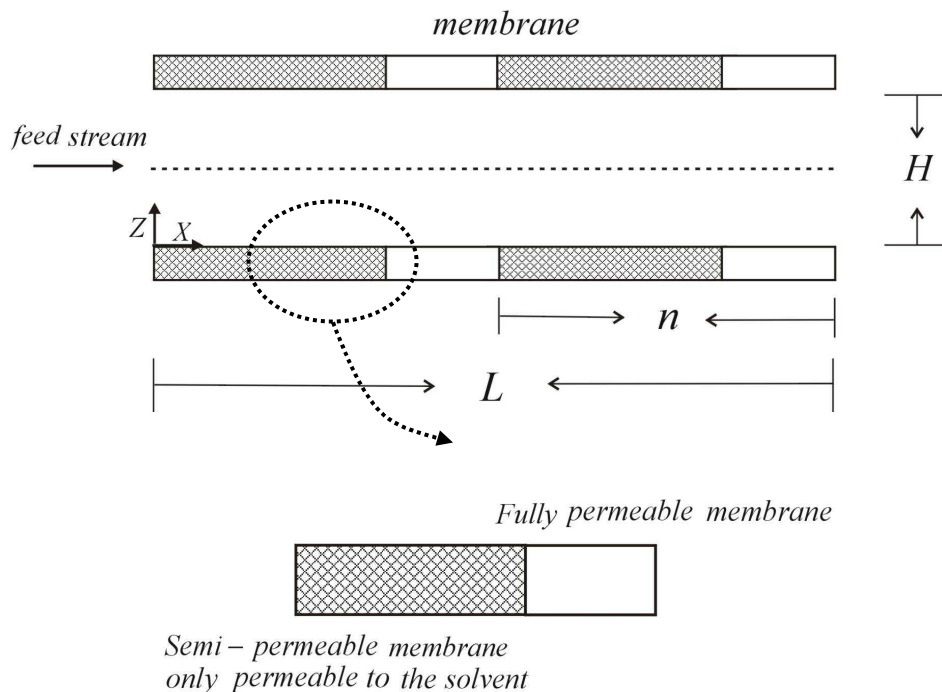


Figure 1.15 – HMC type A (with diffusivity mechanisms).

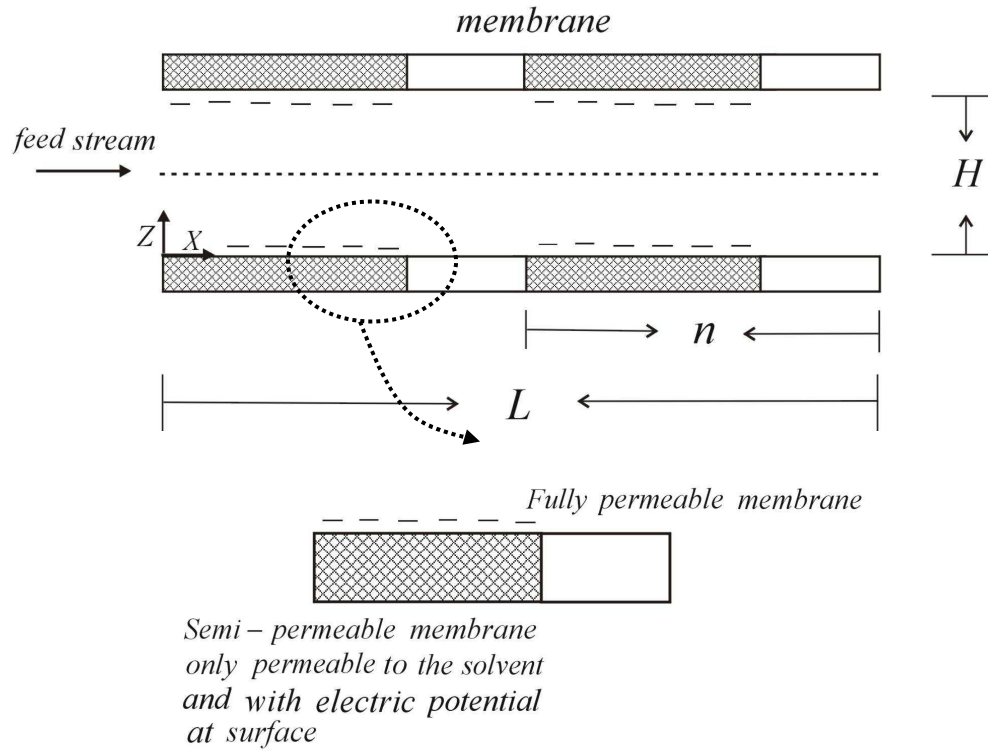


Figure 1.17 – HMC type C (with electric interactions between semi-permeable membranes and components).

1.4. Outline of the thesis

The central content of this thesis is based on 7 scientific papers (some published and some submitted). The thesis reports a strong component in numerical programming to study the advantages of the HMC. Along each chapter (each scientific paper), grid and convergence tests were evaluated to obtain accurate results.

From Chapter 2 to Chapter 5 an in-house numerical code based on finite differences method was used to solve the Mass Transport and Navier-Stokes equations [20, 34-38]. Along these chapters several procedures were successively implemented in the numerical code: separation of two components, variable physical properties and transmission of the components through the semi-permeable membrane. The potential of Hybrid Membrane Cells types A and B was explored through the numerical code developed. Appendix A presents the domain of the HMC and also all the boundary conditions of the conservative equations.

From Chapter 6 to Chapter 8, the coupling between Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations were solved. To obtain convergence of the simultaneous

resolution of the conservative equations, a new finite volume method was developed to solve the Nernst-Planck equations with the electric terms incorporated. Appendix B describes with detail the discretization method of the transport equations. Poisson-Boltzmann and Navier-Stokes equations were solved through finite differences method following the procedure described in [47, 48]. The development of the new numerical method required a complex and extended analysis of convergence of the set of equations to the correct solution. Chapter 6 reports the development of a method with simplified considerations while Chapter 7 and 8 reports the development of this new numerical code without any simplification. The potential of HMC type C was explored through the new numerical code developed.

The outline of the thesis is described chapter by chapter as following:

Chapter 2 describes the advantages of using a new membrane fractionation process based on the combination of hybrid membrane cells and differential diffusion of two solutes (HMC type A). Navier-Stokes and mass transport equations for two components were implemented and solved simultaneously by finite differences method. Concentration and flow fields are described with detail over the membrane. The efficiency of the separation is analyzed through the recovery and purity of the less diffusive component. This chapter was published in an international journal: *Desalination* (Pinto et al., 2009).

Chapter 3 is an improvement study of Chapter 2. Chapter 3 reports a detailed study of the effect of variable transport properties in the separation of two macromolecules - Bovine Serum Albumin(BSA)/Dextran-T10 or BSA/Lysosyme - by differential diffusivity in a hybrid membrane cell (HMC type A). Concentration dependence on the diffusivity of the components and on the viscosity of the solution and non-linear concentration dependence of the osmotic pressure of the solutes are considered and implemented in the numerical code. The differences in the separation numerical results are compared considering variable properties (diffusivity and viscosity) or constant properties (diffusivity and viscosity) with negligible/not negligible osmotic pressure. This chapter was accepted for publication in the international journal *Separation Science and Technology* (Pinto et al., 2011).

Chapter 4 presents a detailed numerical study of the apparent selectivity in the fractionation of BSA (bovine serum albumin) and Dextran-T10 by ultrafiltration. A convective-diffusive transport model across the membrane is adopted and implemented in

the numerical code to simulate the transmission of the components through the membrane. The influence in the selectivity of pressure drop along the cell, permeate velocity along the membrane, build-up of concentration layer over the membrane, variable properties, transmembrane pressure, specific area of the membrane pores, resistance of the membrane (among other parameters) are studied. This chapter was submitted for publication in the *AIChE* journal (Pinto et. al., 2011).

Chapter 5 reports the use of hybrid membrane cells to improve the apparent selectivity in the fractionation of two components. This is achieved by numerical methods. Partial transmission of the solutes is considered in the semi-permeable sub-sections of the hybrid membrane cell through the convective-diffusive transport model across the membrane adopted (HMC type B). The selectivity of the hybrid membrane cell is then compared with the selectivity of a conventional cell under several operational parameters. This chapter was published in an international journal: *Industrial and Engineering Chemistry Research* (Pinto et. al., 2010).

Chapter 6 presents the detailed numerical study to obtain the effect of a charged membrane in the separation of electrically charged components (ionic solution of NaCl). The Poisson-Boltzmann, Navier-Stokes and Nernst-Planck equations are implemented. A new numerical code based on a finite volume method combining with fractional-step method and doner-cell upwind method is developed to solve the Nernst-Planck equations. A simplified approach of Poisson-Boltzmann equation based on finite differences method is considered and solved independently. The resultant electric field is used for the electric terms of Nernst-Planck equations. Concentration profiles along the length of the membrane are compared considering or not electric effects. This chapter was published in an international journal: *Desalination and Water Treatment* (Pinto el. al., 2010).

In **Chapter 7** Poisson-Boltzmann, Navier-Stoke and Nernst-Planck equations are solved without any simplification and all of them with the electric contributions incorporated. Poisson-Boltzmann is solved through a fractional-step method combining with finite differences method. This chapter focuses the coupling between the electric field and the flow field / concentration fields of all the species in solution (macromolecules and charged ions). The new numerical code is validated and applied to the study of the fractionation of molecules through a hybrid membrane cell composed by negatively charged semi-permeable

membranes (HMC type C). This chapter was accepted for publication in the international journal *Desalination and Water Treatment* (Pinto et. al., 2011).

Chapter 8 studies the application of the stagnant film equation to electrophoretic migration of proteins near ultrafiltration membranes. The numerical code developed in Chapter 7 is used to solve the Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations and to evaluate the film equation predictions and the correspondent range of validity. The selectivity of the separation of BSA (bovine serum albumin) and LYS (lysosyme) in an ionic solution of NaCl is compared using film equation predictions and numerical data. This chapter was submitted for publication in the international journal *Chemical Engineering Science* (Pinto et. al., 2011).

Chapter 9 summarizes the general conclusions of this thesis and the suggestions for future work.

1.5. Nomenclature

C	Solute concentration
C_0	Solute concentration in the bulk
C_m	Solute concentration at the membrane surface
c_m	Normalized solute concentration at the membrane surface
$C_m^{uniform}$	Uniform solute concentration at membrane surface
C_p	Permeate solute concentration
D	Molecular diffusivity
H	Distance between parallel plates
k	Solute mass transfer coefficient
k^I	Solute mass transfer coefficient for an impermeable cell
L	Length of the cell
l	Normalized length of the cell
L_m	Total length of the membrane sections
l_m	Total normalized length of the membrane sections
L_s	Length of the semi-permeable membrane sub-section
l_s	Normalized length of the semi-permeable membrane sub-section

L_f	Length of the fully permeable membrane sub-section
l_f	Normalized length of the fully permeable membrane sub-section
L_{in}	Length of the inlet section
l_{in}	Normalized length of the inlet section
L_{out}	Length of the outlet section
l_{out}	Normalized length of the outlet section
$\dot{m}$	Solute mass flux at membrane surface
n	Membrane section
P_{eff}	Effective pressure
P	Static pressure
R_m	Membrane resistance
S_i	Transmission of solute i
V_0	Mean feed velocity
V_m	Permeate velocity
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Z	Vertical coordinate
z	Normalized vertical coordinate

Non-dimensional numbers

Pe	Peclet number
Sh^I	Sherwood number for an impermeable cell
Π_v^0	$\Pi_v^0 = \frac{\Delta P - \Delta \pi_0}{R_m \mu V_0}$
$\Pi_{\Delta \pi_0}$	$\Pi_{\Delta \pi_0} = \frac{\Delta \pi_0}{\Delta P}$
Π_{π_0}	$\Pi_{\pi_0} = \frac{\pi_0^m}{\Delta P}$
Π_v^S	Non-dimensional solvent velocity of a non-polarized semi-permeable membrane
Π_v^f	Non-dimensional concentrate velocity

Greek Symbols

ΔP_{eff}	Effective pressure difference between concentrate and permeate side
ΔP	Static pressure difference across the membrane
ε	Fraction of fully-permeable pores
π	Osmotic pressure
π_0	Feed osmotic pressure
π^m	Osmotic pressure over the membrane
π_0^m	Osmotic pressure over the membrane when concentration at membrane surface is the concentration of the inlet stream
π^p	Osmotic pressure in the permeate
$\Delta\pi$	Osmotic pressure difference ($\Delta\pi = \pi^m - \pi^p$)
$\Delta\pi_0$	Osmotic pressure difference when the concentration over the membrane is the concentration of the inlet stream ($\Delta\pi_0 = \pi_0^m - \pi_0^p$)
δ	Thickness of the boundary layer
σ	Selectivity
μ	Viscosity of the permeate flux

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Chapter 2

A new membrane fractionation process based on the combination of hybrid membrane cells and differential diffusion of two solutes

A new membrane fractionation process based on the combination of hybrid membrane cells and differential diffusion of two solutes was studied by numerical methods. The hybrid membrane cell comprises semi-permeable and fully-permeable membrane sub-sections. While the semi-permeable membranes are permeable to the solvent and impermeable to both solutes, the fully-permeable membranes are permeable to all components of the solution, including the solvent. This cell is used to separate the solute with the lower diffusivity from the solute with the higher diffusivity since the former preferentially accumulates over the surface of the semi-permeable membranes and it is preferentially removed in the fully-permeable sub-sections. The separation is demonstrated by numerical results. The effects of the solvent velocity (velocity of the flow permeating the semi-permeable membranes), concentrate velocity (velocity of the flow permeating the fully-permeable membranes) and the number of sections are studied. In the concentrate stream, the purity of the solute with lower diffusivity increases with the solvent velocity, and decreases with the concentrate velocity. The purity increases slightly with the number of sections.

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2.1. Introduction

Separation processes based on diffusion differences are useful for separating particles or large molecules. The physical support is provided by the different molecular diffusivity of the components (or different Peclet numbers, since the Peclet number is inversely proportional to the molecular diffusivity). There are several separation processes that take advantage of differences in the diffusivity, namely Diffusion Separation [1], Thermal Diffusion Separation [2, 3, 4, 5], Brownian Motors [6], Field Flow Fractionation (FFF) [7, 8, 9] and Split-flow thin-cell (SPLITT) fractionation [10, 11].

Diffusion Separation and Thermal Diffusion Separation can be used to separate isotopes, including the enrichment of uranium [1]. Diffusion Separation requires the use of a porous barrier, across which the component with the higher diffusivity preferentially permeates. Thermal Diffusion Separation separates high molecular mass isotopes from low molecular mass isotopes by taking advantage of the effect of temperature gradients into the diffusivities. Brownian Motors perform the separation of high diffusivity components from low diffusivity components due to a combination of Brownian motion and an anisotropic field. In principle, they can be used to separate large particles from small ones.

In FFF processes, particles are subjected to a laminar (parabolic) fluid flow in the tangential direction and to a field (e.g. gravity, electric fields and magnetic fields) perpendicular to the flow. The position of a molecule in the flow depends on the forces applied in the perpendicular direction and on the diffusivity of the molecule. Molecules with small diffusivity are transported by the main field to the walls of the apparatus, while particles with large diffusivity are transported away from the wall. Since the flow is parabolic, molecules with larger diffusivity have smaller retention times [12].

FFF processes must work in non-steady state and are suitable for analytical separations. They are not suitable for large-scale industrial applications. One example is Flow Field Flow Fractionation (FlFFF), an analytical process, mainly used to test small samples [13]. In an FlFFF process, a solution or suspension is fed to a parallel plate cell with two feed streams. The upper plate is fully-permeable, while the lower plate membrane is permeable only to the solvent. Solutes are transported in the direction of the lower membrane by normal convection and away from the membrane by diffusion. Therefore, high diffusivity

components reach a position far from the membrane, while the low diffusivity components stay closer to the membrane. High diffusivity components are, in equilibrium (normal direction), in a location with a high tangential flow velocity and leave the cell faster.

A technique similar to FFF is Split-flow thin-cell (SPLITT) fractionation. A SPLITT cell is similar to a FFF cell, except that it has a splitter that separates the flowing fluid in the cell into two outflow streams with different compositions: one stream carries the components with higher diffusivity and the other carries those with lower diffusivity.

In this paper we present a new diffusion separation process which combines some characteristics of pressure-driven membrane separation processes and some characteristics of SPLITT and FIFFF processes. Contrary to SPITT and FIFFF, this process has the potential to be used in continuous in large-scale facilities. It takes advantage of the polarization phenomena to fractionate a solution containing two solutes. The separation of the solutes, which must have different diffusivities, is achieved in a hybrid membrane cell that combines alternating sections of fully and semi-permeable membranes.

One example involving the separation of two solutes is protein fractionation. For large-scale applications, pressure driven membrane processes are usually used. Protein fractionation methods are based on the different permeability of the proteins to be separated. For a system with two proteins, the protein with the higher diffusivity diffuses away from the membrane while the other with the lower diffusivity remains concentrated near the membrane surface (concentration polarization phenomena). This phenomenon is considered undesirable since it may reduce the efficiency of the separation process [14]. However, concentration polarization is a state of high separation between the solvent and the solute, and between solutes with different diffusivities. Recently, Miranda and Campos [15] presented a numerical study showing that it is possible to take advantage of the concentration polarization to improve membrane separation processes. They proved that solute purity and permeate velocity increase if hybrid cells combining semi and fully-permeable membrane sections are used.

Hybrid membrane systems combine two membrane unit operations. Usually one unit operation performs a solvent removal operation and the other a solute removal operation [16]. Hybrid membrane cells combine membranes with different properties, frequently alternating in series [15, 17, 18, 19].

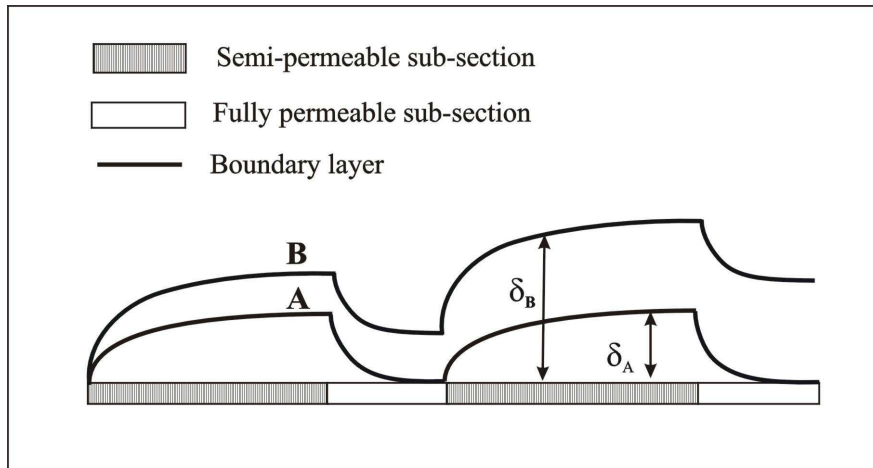


Figure 2.1 – Mass boundary layers for a differential diffusivity process in a hybrid cell.

Figure 2.1 represents the mass transport of two solutes in the hybrid membrane cell proposed in this work. The cell comprises alternate sections of fully and semi-permeable membranes. If the cell is used to treat a solution of two components A and B, two mass boundary layers will be formed, one for each component. The concentration near the membrane depends on the Peclet number of the respective component. The component with lower diffusivity will accumulate in the vicinity of the membrane, while the component with higher diffusivity will diffuse away from the membrane. Since the fluid of the boundary layer is removed in the contiguous fully-permeable sub-section, the fluid leaving the cell through this sub-section will be richer in the component with lower diffusivity.

2.2. Cell description

The hybrid cell under study is schematically represented in Figure 2.2. This cell is the same as the one studied by Miranda and Campos [15]. It is a parallel plate cell with two kinds of membranes alternating along the walls: one semi-permeable (impermeable to the solutes and permeable to the solvent) and another fully permeable (permeable to both solutes and to the solvent). The distance between the walls of the cell is H , the width and length of the cell are W and L , respectively. The feed stream is separated into three streams: a retentate stream and two permeate streams. One of the permeate streams crosses the semi-permeable membranes, and since it is almost pure solvent it is called the solvent stream. The other one crosses the fully permeable membranes, and since it is rich in the solute with the lower diffusivity it is called the concentrate stream. The permeate streams are collected in two

independent permeate chambers: the solvent chamber and the concentrate chamber. The mean velocity of the feed is V_0 , the concentration of solutes A and B at the inlet are C_A^{in} and C_B^{in} , respectively.

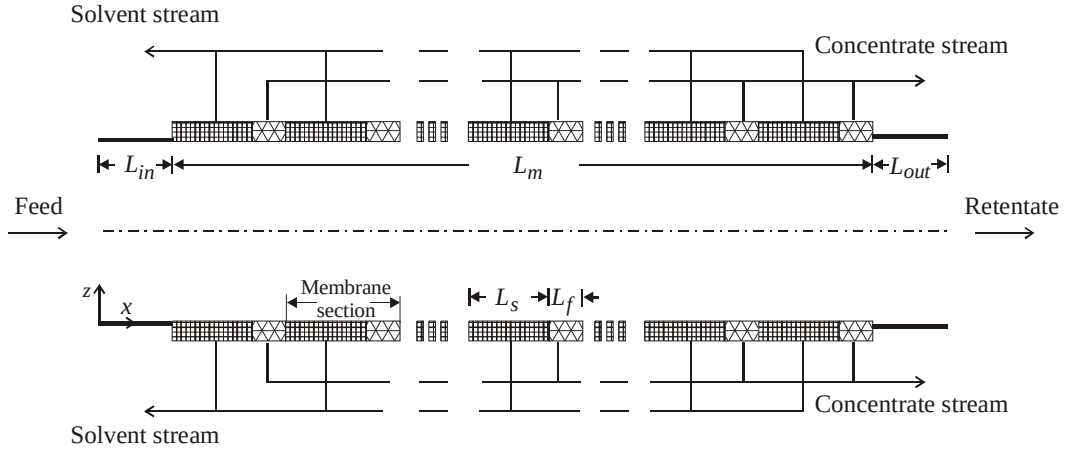


Figure 2.2 - Schematic representation of the hybrid cell. The cell has an inlet section, an outlet section and n membrane sections. Each membrane section has a semi-permeable sub-section and a fully permeable sub-section. In the permeate side, the cell has two independent collectors, one for the fluid that crosses the semi-permeable membranes and another for the fluid that crosses the fully permeable membranes.

The cell is divided into the inlet section, the outlet section and the n membrane sections. The length of the inlet section is L_{in} , the total length of all membrane sections is L_m and the length of the outlet section is L_{out} . The inlet and the outlet sections are both impermeable to the solutes and to the solvent. Each membrane section includes a semi-permeable membrane sub-section and a fully permeable membrane sub-section. Semi-permeable and fully permeable membrane sub-sections are numbered from 1 to n . The length of a semi-permeable sub-section is L_s and the length of a fully permeable sub-section is L_f . The geometric variables normalized by the distance between plates (H) are:

$$l = \frac{L}{H}, l_m = \frac{L_m}{H}, l_{in} = \frac{L_{in}}{H}, l_{out} = \frac{L_{out}}{H}, l_s = \frac{L_s}{H}, l_f = \frac{L_f}{H} \quad (2.1)$$

Since the solute concentrations in the concentrate stream (C_A^f and C_B^f) the solvent stream velocity (V_m^s) and the solute concentrations at the surface of the semi-permeable sub-sections

(C_A^s and C_B^s) may change along the length of each membrane section and from membrane section to membrane section, it is necessary to define mean variables:

- The mean solute concentrations of the concentrate stream for section i , $(\overline{C_A^f})_i$ and $(\overline{C_B^f})_i$

$$(\overline{C_A^f})_i = \frac{\int_0^{L_f} (C_A^f)_m(X_f, 0) V_Z(X_f, 0) dX_f}{\int_0^{L_f} V_Z(X_f, 0) dX_f}; (\overline{C_B^f})_i = \frac{\int_0^{L_f} (C_B^f)_m(X_f, 0) V_Z(X_f, 0) dX_f}{\int_0^{L_f} V_Z(X_f, 0) dX_f} \quad (2.2)$$

where X_f is the longitudinal coordinate originating at the beginning of the fully permeable sub-section i .

- The mean solute concentrations of the concentrate stream for the entire cell, $\overline{C_A^f}$ and $\overline{C_B^f}$, are equal to the arithmetic mean of the mean solute concentration in the concentrate of the sub-sections,

$$\overline{C_A^f} = \frac{\sum_{i=1}^n (\overline{C_A^f})_i}{n}; \overline{C_B^f} = \frac{\sum_{i=1}^n (\overline{C_B^f})_i}{n} \quad (2.3)$$

- The mean velocity of the solvent stream for sub-section i , $(\overline{V_m^s})_i$

$$(\overline{V_m^s})_i = \frac{\int_0^{L_s} V_Z(X_s, 0) dX_s}{\int_0^{L_s} dX_s} \quad (2.4)$$

where X_s is the longitudinal coordinate originating at the beginning of the semi-permeable sub-section i .

- The mean velocity of the solvent stream for the entire cell, $\overline{V_m^s}$, is equal to the arithmetic mean of the mean solvent velocity in the sub-sections:

$$\overline{V_m^s} = \frac{\sum_{i=1}^n \left(\overline{V_m^s} \right)_i}{n} \quad (2.5)$$

- The mean solute concentrations at the surface of the semi-permeable membrane of section i , $\left(\overline{C_A^s} \right)_i$ and $\left(\overline{C_B^s} \right)_i$, are given by

$$\left(\overline{C_A^s} \right)_i = \frac{\int_0^{L_s} \left(C_A^s \right)_m (X_s, 0) V_Z (X_s, 0) dX_s}{\int_0^{L_s} V_Z (X_s, 0) dX_s}; \quad \left(\overline{C_B^s} \right)_i = \frac{\int_0^{L_s} \left(C_B^s \right)_m (X_s, 0) V_Z (X_s, 0) dX_s}{\int_0^{L_s} V_Z (X_s, 0) dX_s} \quad (2.6)$$

- The mean solute concentrations at the surface of all semi-permeable membranes, $\overline{C_A^s}$ and $\overline{C_B^s}$, are equal to the arithmetic mean of the mean solute concentration in the sub-sections:

$$\overline{C_A^s} = \frac{\sum_{i=1}^n \left(\overline{C_A^s} \right)_i}{n}; \quad \overline{C_B^s} = \frac{\sum_{i=1}^n \left(\overline{C_B^s} \right)_i}{n} \quad (2.7)$$

Henceforth, the velocities will be normalized by the mean feed velocity, V_0 , the concentration of A by the feed concentration C_0^A and the concentration of B by the feed concentration C_0^B (these dimensionless variables are written in lowercase letters).

Supported by the previous mean parameters, it is possible to define a measure of the separation degree between components A and B. The purity of A in relation to B, $p_{A/B}$, is defined as:

$$p_{A/B} = \frac{c_A}{c_A + c_B \frac{C_B^{in}}{C_A^{in}}} \quad (2.8)$$

Therefore, the mean purity of A (at the concentrated stream) for the fully-permeable sub-section i , $\left(\overline{p_{A/B}} \right)_i$, is:

$$\left(\overline{p}_{A/B}^f\right)_i = \frac{\left(\overline{c}_A^f\right)_i}{\left(\overline{c}_A^f\right)_i + \left(\overline{c}_B^f\right)_i \frac{C_B^{in}}{C_A^{in}}} \quad (2.9)$$

The mean purity of A for all fully-permeable sub-sections in the cell, $\overline{p}_{A/B}^f$, is:

$$\overline{p}_{A/B}^f = \frac{\overline{c}_A^f}{\overline{c}_A^f + \overline{c}_B^f \frac{C_B^{in}}{C_A^{in}}} \quad (2.10)$$

The mean purity of A over a semi-permeable membrane is:

$$p_{A/B}^s = \frac{c_A^s}{c_A^s + c_B^s \frac{C_B^{in}}{C_A^{in}}} \quad (2.11)$$

The mean purity of A (at the membrane surface) for the semi-permeable sub-section i , $\left(\overline{p}_{A/B}^s\right)_i$, is:

$$\left(\overline{p}_{A/B}^s\right)_i = \frac{\left(\overline{c}_A^s\right)_i}{\left(\overline{c}_A^s\right)_i + \left(\overline{c}_B^s\right)_i \frac{C_B^{in}}{C_A^{in}}} \quad (2.12)$$

The mean purity of A for all semi-permeable sub-sections in the cell, $\overline{p}_{A/B}^s$, is:

$$\overline{p}_{A/B}^s = \frac{\overline{c}_A^s}{\overline{c}_A^s + \overline{c}_B^s \frac{C_B^{in}}{C_A^{in}}} \quad (2.13)$$

The purity of the feed stream, $p_{A/B}^{in}$ is:

$$p_{A/B}^{in} = \frac{C_A^{in}}{C_A^{in} + C_B^{in}} = \frac{1}{1 + \frac{C_B^{in}}{C_A^{in}}} \quad (2.14)$$

Another important parameter for quantifying separation is the recovery of solute A in the cell, Rec_A , i.e., the fraction of A of the feed stream recovered in the concentrate stream:

$$Rec_A = 2 \varepsilon l_m v_m^f \bar{c}_A^f \quad (2.15)$$

with ε defined by:

$$\varepsilon = \frac{l_f}{l_s + l_f} \quad (2.16)$$

2.3. Numerical Methods

The flow and the mass transport in the cell were studied by numerical methods. The conservation equations, domain and respective boundary conditions were selected. The equations were discretized by the finite difference method and numerically solved to obtain the flow and concentration fields.

2.3.1. Domain and numerical grid

As explained in Miranda and Campos [15], the number of grid nodes needed to accurately solve the flow and mass transport equations increases with the number of membrane sections. For this reason, this work used the composite grid method referred by Miranda and Campos [15].

2.3.2. Equations and boundary conditions

Then flow in the cell is described by Navier–Stokes equations. For a bi-dimensional cell, the dimensionless Navier–Stokes equations can be written for secondary variables (vorticity, ω , and stream function, ψ) and Cartesian coordinates (x and z).

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} \quad (2.17)$$

$$v_x \frac{\partial \omega}{\partial x} + v_z \frac{\partial \omega}{\partial z} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial z^2} \right) \quad (2.18)$$

$$v_x = \frac{\partial \psi}{\partial z} \quad (2.19)$$

$$v_z = -\frac{\partial \psi}{\partial x} \quad (2.20)$$

In the equations, x represents the normalized longitudinal direction, z the normalized transversal direction and Re the Reynolds number based on the mean inlet velocity and on the height of the parallel plate cell:

$$\text{Re} = \frac{\rho V_0 H}{\mu} \quad (2.21)$$

where ρ is the fluid density and μ the fluid viscosity.

The dimensionless mass transport equations in Cartesian coordinates for solutes A and B are:

$$\begin{cases} v_x \frac{\partial c_A}{\partial x} + v_z \frac{\partial c_A}{\partial z} = \frac{1}{\text{Pe}_A} \left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial z^2} \right) \\ v_x \frac{\partial c_B}{\partial x} + v_z \frac{\partial c_B}{\partial z} = \frac{1}{\text{Pe}_B} \left(\frac{\partial^2 c_B}{\partial x^2} + \frac{\partial^2 c_B}{\partial z^2} \right) \end{cases} \quad (2.22)$$

where Pe_A and Pe_B are the Peclet numbers of the solutes A and B respectively:

$$\text{Pe}_A = \frac{V_0 H}{D_A}; \text{Pe}_B = \frac{V_0 H}{D_B} \quad (2.23)$$

where D_A and D_B are the molecular diffusivities of the solutes A and B respectively.

The mass transport equations were solved by the so-called ϕ method [20]. In this method, a variable transformation $\phi = \ln(c)$ is used to linearize the concentration gradients in the mass boundary layer over the membrane. Then, the mass transport equations are converted into the ϕ transport equations:

$$\begin{cases} v_x \frac{\partial \phi_A}{\partial x} + v_z \frac{\partial \phi_A}{\partial z} = \frac{1}{\text{Pe}_A} \left(\frac{\partial^2 \phi_A}{\partial x^2} + \frac{\partial^2 \phi_A}{\partial z^2} + \frac{\partial \phi_A}{\partial x} \frac{\partial \phi_A}{\partial x} + \frac{\partial \phi_A}{\partial z} \frac{\partial \phi_A}{\partial z} \right) \\ v_x \frac{\partial \phi_B}{\partial x} + v_z \frac{\partial \phi_B}{\partial z} = \frac{1}{\text{Pe}_B} \left(\frac{\partial^2 \phi_B}{\partial x^2} + \frac{\partial^2 \phi_B}{\partial z^2} + \frac{\partial \phi_B}{\partial x} \frac{\partial \phi_B}{\partial x} + \frac{\partial \phi_B}{\partial z} \frac{\partial \phi_B}{\partial z} \right) \end{cases} \quad (2.24)$$

Boundary conditions have been presented by Miranda and Campos [15, 20, 21, 22]. However, the boundary conditions for the semi-permeable membrane used by Miranda and Campos [15] can not be applied in this study because the osmotic pressure has the contribution of both solutes A and B:

$$\pi = k_A C_A^{\text{in}} c_A + k_B C_B^{\text{in}} c_B \quad (2.25)$$

where, k_A and k_B are the first virial coefficients of A and B, respectively.

This dependence implies that the velocity condition for boundary V is:

$$-v_z = \frac{\Pi_v}{1 - \Pi_{\pi_0}^A - \Pi_{\pi_0}^B} \left[1 - \Pi_{\pi_0}^A C_m^A - \Pi_{\pi_0}^B C_m^B \right] \quad (2.26)$$

where, c_m is the normalized concentration at the surface of the semi-permeable membrane. The dimensionless numbers in the equation are defined in the following way:

$$\Pi_{\pi_0}^A = \frac{\pi_0^A}{\Delta P_m} \quad (2.27)$$

$$\Pi_{\pi_0}^B = \frac{\pi_0^B}{\Delta P_m} \quad (2.28)$$

$$\Pi_v = \frac{\Delta P_m - (\pi_o^A + \pi_o^B)}{V_o R_m} \quad (2.29)$$

The physical meaning of these dimensionless groups is described in detail by Miranda and Campos [21]. Briefly, Π_v represents the ratio between the permeate velocity through a non-polarized membrane and the mean velocity at the cell inlet, and Π_{π_0} the ratio between the osmotic pressure over a non-polarized membrane and the static pressure difference across the membrane.

All the boundary conditions for the boundary of the semi-permeable membranes are given in Table 2.1.

Table 2.1- Boundary conditions for the semi-permeable membranes.

Semi-permeable membranes
$v_x = 0$
$-v_z = \frac{\Pi_v^s}{1 - \Pi_{\pi_0}^A - \Pi_{\pi_0}^B} \left[1 - \Pi_{\pi_0}^A c_m^A - \Pi_{\pi_0}^B c_m^B \right]$
$\psi = -\frac{1}{2} + \int -v_z dx$
$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$
$-\frac{1}{Pe} \frac{\partial c}{\partial z} = v_z c$
$-\frac{1}{Pe} \frac{\partial \phi}{\partial z} = v_z$

2.3.3. Grid tests

The accuracy of the grid used to solve the discretized equations was studied by performing several tests. The number of nodes in the longitudinal direction of each semi-permeable sub-section (ni_s), the number of nodes in the longitudinal direction of each fully

permeable sub-section (ni_f) and the number of nodes in the vertical direction n_j were increased in a pre-defined scheme. The numerical error was determined by:

$$\varepsilon_{\bar{C}_A^f} = \left| \frac{\left(\bar{C}_A^f \right)_{ref} - \bar{C}_A^f}{\left(\bar{C}_A^f \right)_{ref}} \right| \quad (2.30)$$

where $\left(\bar{C}_A^f \right)_{ref}$ is the mean concentration of the concentrate stream for the densest grid (reference grid - 641×501 nodes).

The operation conditions selected to perform the tests are those for which the concentration gradients are higher ($\Pi_{\pi_0} = 0$; $\Pi_v^s = 10^{-4}$; $\Pi_v^f = 10^{-4}$; $l_m = 100$; $\varepsilon = 0.1$; $Pe = 10^6$). The results are in Table 2.2 and in Figure 2.3. The decrease and the low values obtained for the error (3.6% grid I and 1.3 % grid II) confirm the accuracy of the grid used (321×251). Figure 2.4 confirms that the normalized solute concentration, in the last section of the cell ($n = 8$), is practically the same whatever is the mesh grid used.

Table 2.2 - Grid tests for $n = 8$.

Grid		ni_s	ni_f	n_j	ε_p (%)
I	161x126	100	20	126	3.6
II	321x251	200	40	251	1.3
III	641x501	400	80	501	<i>reference grid</i>

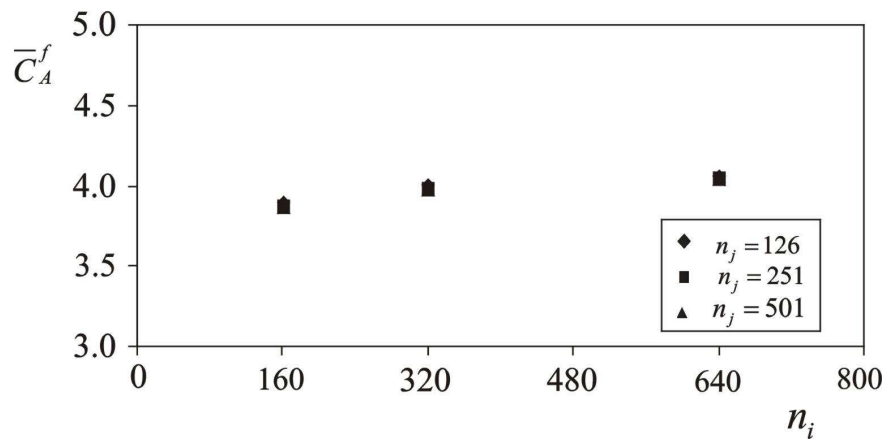


Figure 2.3 – Values of mean purity of the concentrate for different grids

($p_{A/B}^{in} = 50\%$, $n = 8$, $\Pi_{\pi_0} = 0$; $\Pi_v^s = 10^{-4}$; $\Pi_v^f = 10^{-4}$; $l_m = 100$; $\varepsilon = 0.1$; $Pe = 10^6$).

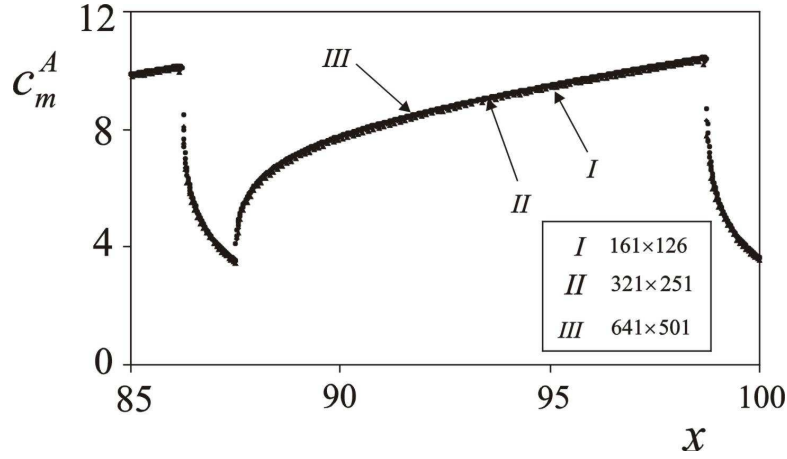


Figure 2.4 – Normalized solute concentration at the membrane surface for the last sub-section

$$(P_{A/B}^{in} = 50\%, n = 8, \Pi_{\pi_0} = 0; \Pi_v^s = 10^{-4}; \Pi_v^f = 10^{-4}; l_m = 100; \varepsilon = 0.1; \text{Pe} = 10^6).$$

2.3.4. Convergence

The convergence of the numerical method was determined based on the residual of the mass transport equation and on the evolution of the error in the concentration in a critical point near the end of the last semi-permeable sub-section.

The residual of the mass transport equation was determined by:

$$R_\phi^A = \sum_{i=2}^{n-1} \sum_{j=2}^{m-1} (R_\phi^A)_{i,j} \quad (2.31)$$

where $(R_\phi^A)_{i,j}$ is given by:

$$(R_\phi^A)_{i,j} = v_x \frac{\partial \phi_A}{\partial x} + v_z \frac{\partial \phi_A}{\partial z} - \frac{1}{\text{Pe}_A} \left(\frac{\partial^2 \phi_A}{\partial x^2} + \frac{\partial^2 \phi_A}{\partial z^2} + \frac{\partial \phi_A}{\partial x} \frac{\partial \phi_A}{\partial x} + \frac{\partial \phi_A}{\partial z} \frac{\partial \phi_A}{\partial z} \right) \quad (2.32)$$

The error of the concentration on a critical location was determined by:

$$\varepsilon_{crit} = \left| \frac{(C_A)_{crit}^k - (C_A)_{crit}^{k-1}}{(C_A)_{crit}^k} \right| \quad (2.33)$$

where *crit* refers to the critical position and *k* to the current time step.

The typical evolutions of the residual and of the error in the concentration are represented in Figure 2.5. Results show that the iterative method converges to a constant concentration and, at the same time, the residual decreases until it reaches a very small value. The following criteria were chosen for convergence:

$$\begin{cases} \varepsilon_{crit} < 10^{-3} \\ R_{\phi} < 10^{-4} \end{cases} \quad (2.34)$$

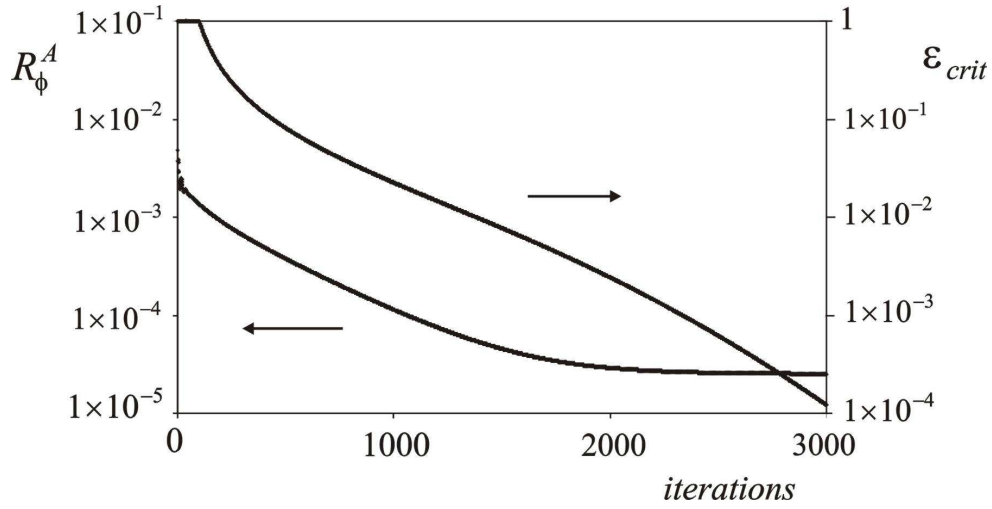


Figure 2.5 – Residue of ϕ and error of the concentration at a critical position as a function of the number of iterations ($\Pi_{\pi_0} = 0$; $\Pi_v^s = 10^{-4}$; $\Pi_v^f = 10^{-4}$; $l_m = 100$; $\varepsilon = 0.1$; $Pe = 10^6$).

2.3.5. Numerical method for an infinite number of membrane sections

As shown by Miranda and Campos [15], the efficiency of a hybrid membrane cell increases as the number of sections increase. Therefore, there is great interest in studying the cell for the theoretical limit of the infinite number of sections. This case has a physical meaning since a cell with an infinite number of sections is equivalent to a cell having a single membrane with two kinds of pores: those which are fully-permeable and those which are permeable to the solvent but impermeable to the solutes. The flow and mass transport in this type of cell were numerically obtained by solving the flow and mass transport equations. Two boundary conditions were reformulated: one for the normal velocity at the membrane surface and another for the solute concentration at the membrane surface (Table 2.3). The

velocity boundary condition must take into account the contribution of both solutes to the osmotic pressure (see ref. [15] for details):

$$-v_z = \frac{\Pi_v^s}{1 - \Pi_{\pi_0}^A - \Pi_{\pi_0}^B} \left[1 - \Pi_{\pi_0}^A c_A(x,0) - \Pi_{\pi_0}^B c_B(x,0) \right] (1 - \varepsilon) + \Pi_v^f \varepsilon \quad (2.35)$$

where ε is the fraction of membrane containing fully-permeable pores.

The boundary condition for the concentration is given by:

$$\Pi_v^f \varepsilon c(x,0) = -v_z(x,0) c(x,0) + \frac{1}{Pe} \frac{\partial c}{\partial z} \quad (2.36)$$

This equation applied to each solute, after combination with the velocity boundary condition, gives:

$$\frac{\Pi_v^s}{1 - \Pi_{\pi_0}^A - \Pi_{\pi_0}^B} \left[1 - \Pi_{\pi_0}^A c_A(x,0) - \Pi_{\pi_0}^B c_B(x,0) \right] (1 - \varepsilon) c_A(x,0) = -\frac{1}{Pe_A} \frac{\partial c_A}{\partial z} \quad (2.37)$$

$$\frac{\Pi_v^s}{1 - \Pi_{\pi_0}^A - \Pi_{\pi_0}^B} \left[1 - \Pi_{\pi_0}^A c_A(x,0) - \Pi_{\pi_0}^B c_B(x,0) \right] (1 - \varepsilon) c_B(x,0) = -\frac{1}{Pe_B} \frac{\partial c_B}{\partial z} \quad (2.38)$$

Table 2.3 - Boundary conditions for a membrane with an infinite number of sections.

Membrane with an infinite number of sections
$v_x = 0$
$-v_z = \frac{\Pi_v^s}{1 - \Pi_{\pi_0}^A - \Pi_{\pi_0}^B} \left[1 - \Pi_{\pi_0}^A c^A(x,0) - \Pi_{\pi_0}^B c^B(x,0) \right] (1 - \varepsilon) + \Pi_v^f \varepsilon$
$\psi = -\frac{1}{2} + \int -v_z dx$
$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$
$\Pi_v^f \varepsilon c(x,0) = -v_z(x,0) c(x,0) + \frac{1}{Pe} \frac{\partial c}{\partial z}$
$-\frac{1}{Pe} \frac{\partial \phi}{\partial z} = -v_z - \Pi_v^f \varepsilon$

2.4. Results and discussion

2.4.1. Concentration and flow fields

Numerical simulations were made for the separation of a solution with two solutes, A and B (A is the component with the lower diffusivity). The operating conditions were: $Pe_A=10^6$, $Pe_B=5 \times 10^5$, $l_m=100$, $\Pi_v^s = 10^{-4}$, $\Pi_v^f = 10^{-4}$, $\Pi_{\pi_0}^A = 0$ and $\Pi_{\pi_0}^B = 0$ (i.e. supposing negligible osmotic pressure for both solutes).

Figures 2.6 to 2.8 help the physical understanding of the separation process described in this work. Figure 2.6 shows the flow field and the iso-concentration lines for components A and B. Since component A has the lower diffusivity, its concentration is higher in the vicinity of the membrane. The streamlines of the fluid leaving the cell through the fully permeate sub-section cross a region rich in this component and poor in component B. Therefore, the concentrate stream is richer in the component with the lower diffusivity (A).

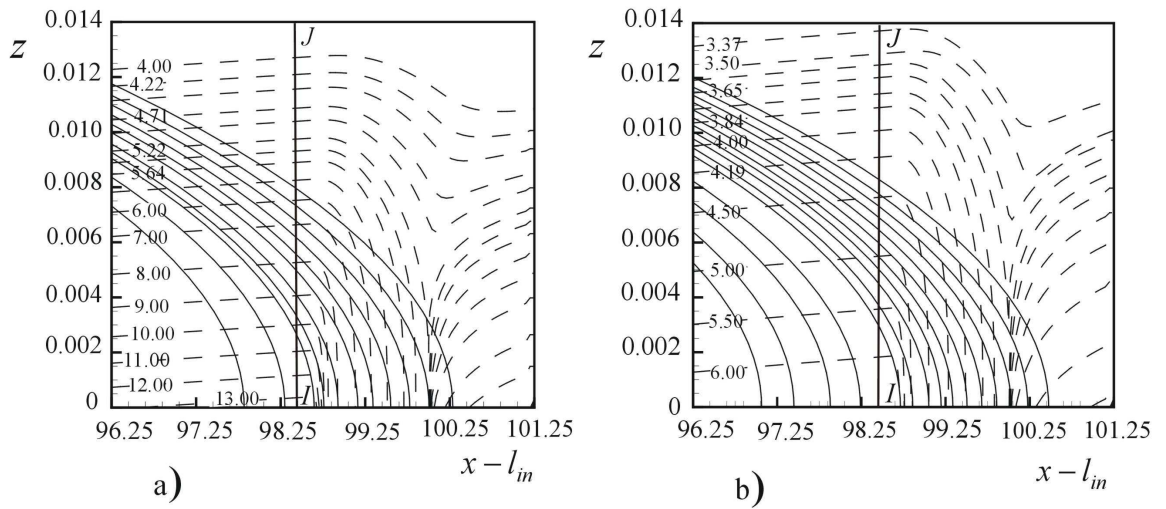


Figure 2.6 - Streamlines (solid) and iso-concentration lines (dotted) in the vicinity of the membrane at the end of the 8th section ($p_{A/B}^{in} = 50\%$, $n=8$, $Pe_A=10^6$, $Pe_B=5 \times 10^5$, $l_m=100$, $\varepsilon=0.1$, $\Pi_v^s=10^{-4}$, $\Pi_v^f=10^{-4}$, $\Pi_{\pi_0}^A=0$ and $\Pi_{\pi_0}^B=0$); a) for the component with the lower diffusivity (A); b) for the component with the higher diffusivity (B).

For a better visualization, the concentrations of A and B along the line I-J (Figure 2.6) are represented in Figure 2.7. The cross-section represented by line I-J is crossed by all the

fluid (see streamlines) that forms the concentrate stream. Along this cross-section, the concentration of the component with the lower diffusivity (A) is higher than the concentration of the component B. This pattern is maintained along all the trajectories of the fluid until it crosses the fully-permeable membrane (Figure 2.8).

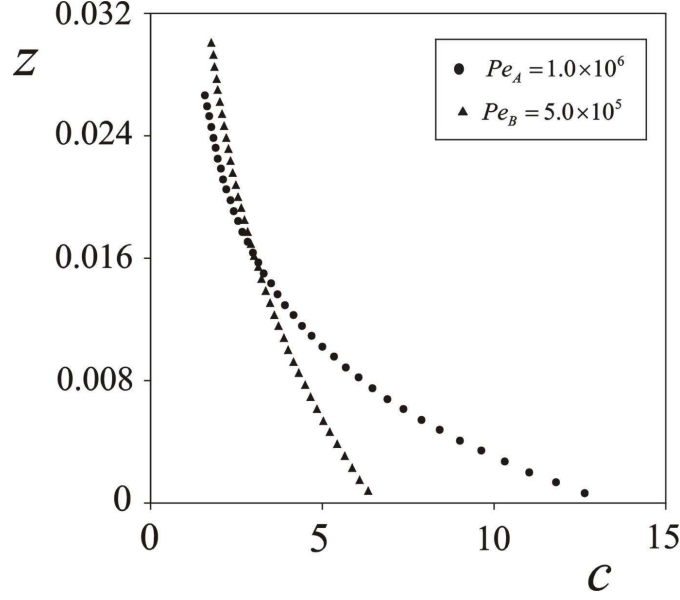


Figure 2.7 - Concentration profiles along z [$x = 98.5$] ($p_{A/B}^{in} = 50\%$, $n = 8$, $Pe_A = 10^6$, $Pe_B = 5 \times 10^5$,

$$l_m = 100, \varepsilon = 0.1, \Pi_v^s = 10^{-4}, \Pi_v^f = 10^{-4}, \Pi_{\pi_0}^A = 0 \text{ and } \Pi_{\pi_0}^B = 0).$$

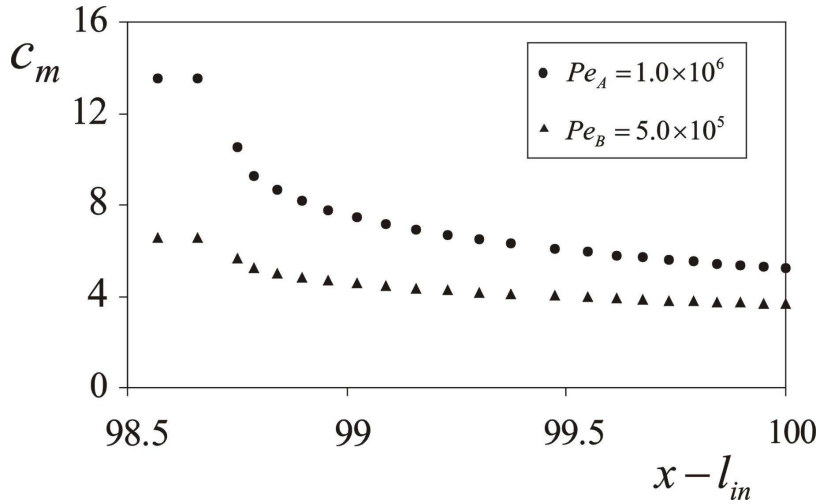


Figure 2.8 - Solute concentration along the fully permeable membrane ($p_{A/B}^{in} = 50\%$, $n = 8$, $l_m = 100$,

$$\varepsilon = 0.1, \Pi_v^s = 10^{-4}, \Pi_v^f = 10^{-4}, \Pi_{\pi_0}^A = 0 \text{ and } \Pi_{\pi_0}^B = 0).$$

Figure 2.8 shows the evolution of the concentration in the last fully permeable sub-section ($n = 8$), for each component in study.

2.4.2. Recovery and productivity

To stress the significant separation and recovery by diffusivity differences in hybrid membranes, the effect of the feed purity ($p_{A/B}^{\text{in}}$) on $\bar{p}_{A/B}^f$ was computed. Figure 2.9 represents the mean purity in the concentrated steam of the component with lower diffusivity as a function of the feed purity for different pairs of Peclet numbers. The vertical distance between the diagonal and each curve is a measure of the separation

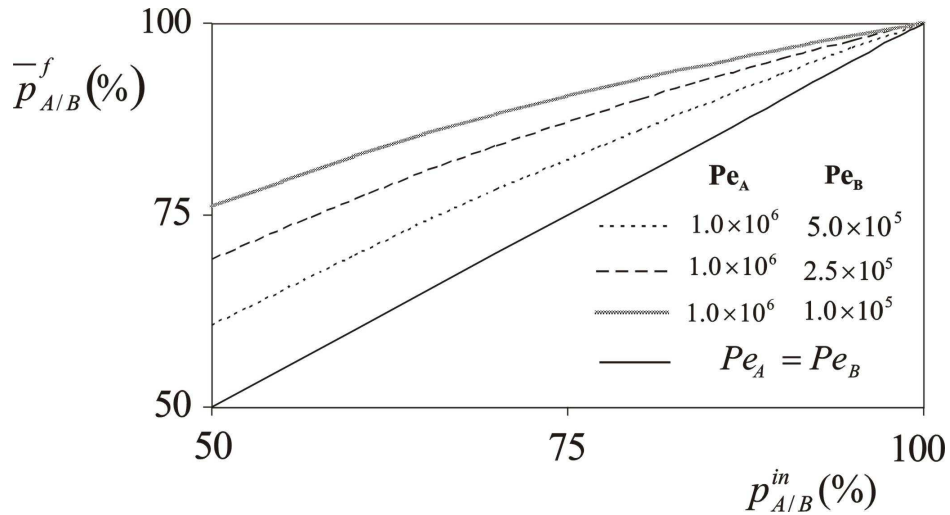


Figure 2.9 - Mean purity of solute A as a function of the feed purity ($n = 8, l_m = 100, \varepsilon = 0.1,$

$$\Pi_v^s = 10^{-4}, \Pi_v^f = 10^{-4}, \Pi_{\pi_0}^A = 0 \text{ and } \Pi_{\pi_0}^B = 0).$$

A deep analysis of the flow and concentration fields in Figure 2.6 put into evidence several ways to increase $\bar{p}_{A/B}^f$. This can be done by increasing the purity of A over the semi-permeable membrane or by restricting the concentrate stream to the fluid that crosses the lower regions of the boundary layer. The purity over the semi-permeable membranes can be increased by manipulating the solvent velocity (Π_v^s). The fluid from the higher regions of the boundary layer can be excluded from the concentrate stream by decreasing the concentrate velocity (Π_v^f) or by shortening the length of the fully permeable sub-sections.

2.4.3. Influence of Π_v^S

When the permeate velocity is zero, none of the solutes has a boundary layer. As the permeate velocity increases, the solutes are dragged into the membrane surface where the solute with the lower diffusivity has a higher concentration. The essential features of this effect are captured by the simplest model to describe a mass boundary layer: the film model. Whereas this model is too simplistic to capture the mechanism of mass transport in the vicinity of the membrane because it ignores mass transport by convection in the tangential direction, the effect of the permeate velocity in the purity over the membrane is qualitatively well-described by the film model. Furthermore, since the film equation is particularly accurate for small values of the permeate velocity and of the Peclet number, it can be used to estimate the purity at the membrane surface. When $\Pi_{\pi_0}^A = 0$ and $\Pi_{\pi_0}^B = 0$ (negligible osmotic pressure effect), the film equation for each solute is:

$$v_m = \Pi_v^s = \frac{\text{Sh}_A^{\text{ln}}}{\text{Pe}_A} \ln(c_m^A); \quad v_m = \Pi_v^s = \frac{\text{Sh}_B^{\text{ln}}}{\text{Pe}_B} \ln(c_m^B) \quad (2.39)$$

where Sh_A^{ln} is the Sherwood number based on the film equation. For low values of Π_v^s and Peclet number, Sh_A^{ln} is accurately estimated by the Sherwood number of an impermeable cell with soluble walls [22]:

$$\text{Sh}^{\text{imp}} = a \text{Pe}^{1/3} \left(\frac{1}{x} \right)^{1/3} \quad (2.40)$$

In these conditions, the concentration of the solutes at the membrane surface is given by:

$$c_m^A = \exp \left[\frac{1}{a} \Pi_v \text{Pe}_A^{2/3} \left(\frac{1}{x} \right)^{-1/3} \right]; \quad c_m^B = \exp \left[\frac{1}{a} \Pi_v \text{Pe}_B^{2/3} \left(\frac{1}{x} \right)^{-1/3} \right] \quad (2.41)$$

The purity over the membrane is then

$$p_{A/B}^s = \frac{1}{1 + e^{\frac{\Pi_v}{x^{-1/3}a} (\text{Pe}_B^{2/3} - \text{Pe}_A^{2/3})} \frac{C_B^{\text{in}}}{C_A^{\text{in}}}} \quad (2.42)$$

This equation shows that an increase of Π_v^s affects the concentration fields of the solutes and the outcome is an increase of the purity over the semi-permeable membranes.

Numerical data confirm that the mean purity of the concentrated stream, $\bar{p}_{A/B}^f$, increases with increasing Π_v^s (Figure 2.10), as well as the recovery of the component A (Figure 2.11).

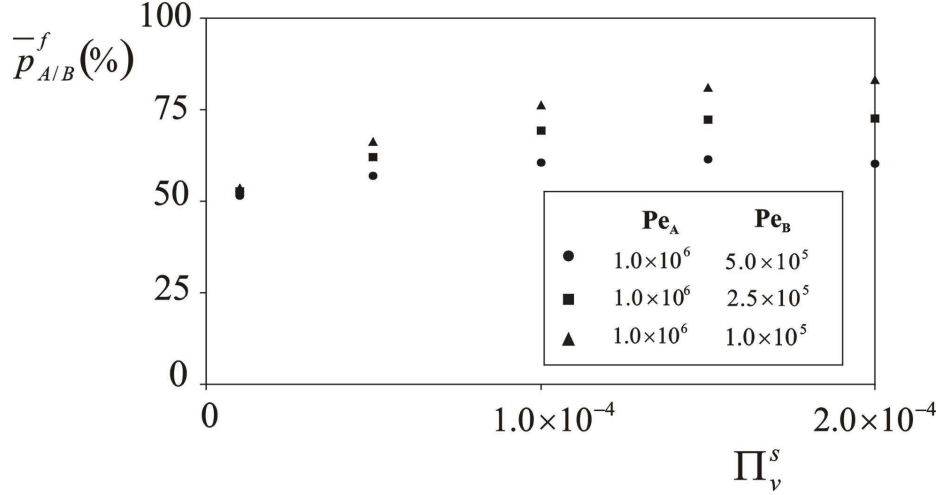


Figure 2.10 – Mean purity in the concentrate stream of the solute with the lower diffusivity as a function of Π_v^s , for different pairs of values of Peclet number ($p_{A/B}^{in} = 50\%$, $n = 8$, $l_m = 100$, $\varepsilon = 0.1$, $\Pi_v^f = 10^{-4}$, $\Pi_{\pi_0}^A = 0$ and $\Pi_{\pi_0}^B = 0$).

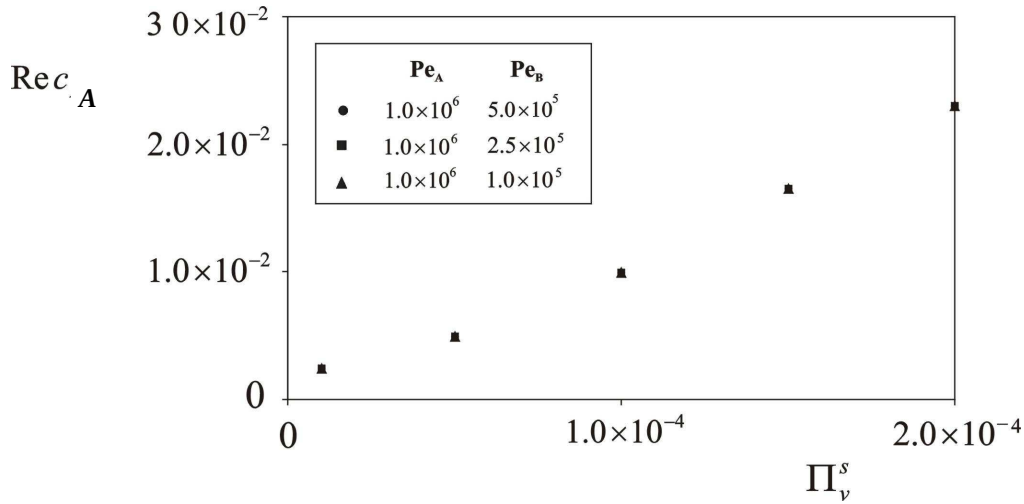


Figure 2.11 - Recovery of component A as a function of Π_v^s ($p_{A/B}^{in} = 50\%$, $n = 8$, $l_m = 100$, $\varepsilon = 0.1$, $\Pi_v^f = 10^{-4}$, $\Pi_{\pi_0}^A = 0$ and $\Pi_{\pi_0}^B = 0$).

2.4.4. Influence of Π_v^f

For low concentrate stream velocities (Π_v^f), most of the concentrate stream comes from the lower regions of the boundary layer over the membrane where the purity of A is high. The outcome is a concentrate stream of high purity. At the limit, when Π_v^f converges to zero, the purity converges to a plateau. The exact value of this plateau can be determined by simulating the cell for $\Pi_v^f = 0$ (impermeable sub-section).

As the velocity of the concentrate stream increases more and more fluid comes from the region where purity of A is lower and therefore the purity of the concentrate stream decreases. Purity of A converges to its value in the bulk (Figure 2.12).

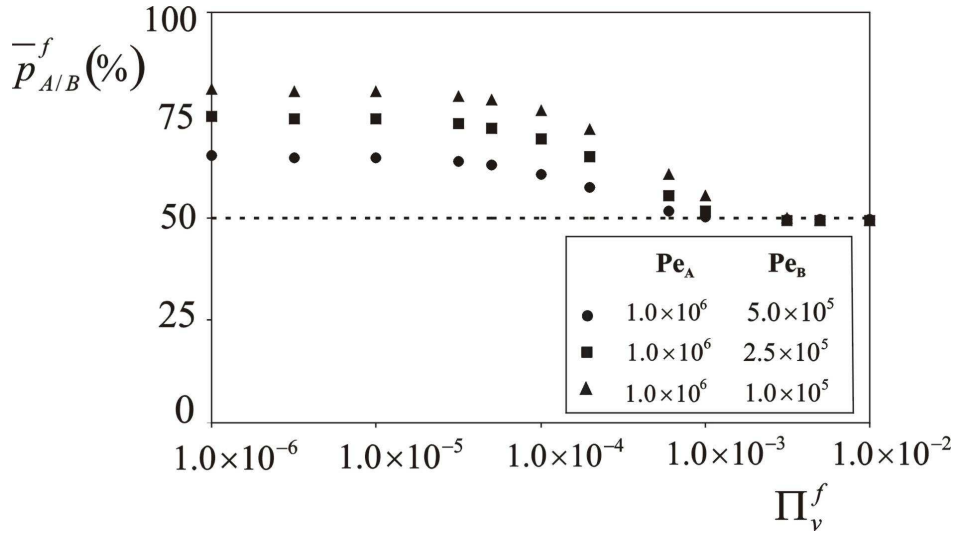


Figure 2.12 - Mean purity of the solute with the lowest diffusivity as a function of Π_v^f for different pairs of Peclet numbers ($p_{A/B}^{in} = 50\%$, $n = 8$, $l_m = 100$, $\varepsilon = 0.1$, $\Pi_v^s = 10^{-4}$, $\Pi_{\pi_0}^A = 0$ and $\Pi_{\pi_0}^B = 0$).

The increased purity of the concentrate stream obtained by decreasing the concentrate velocity has an important drawback: the recovery of the solute decreases as is shown in Figure 2.13.

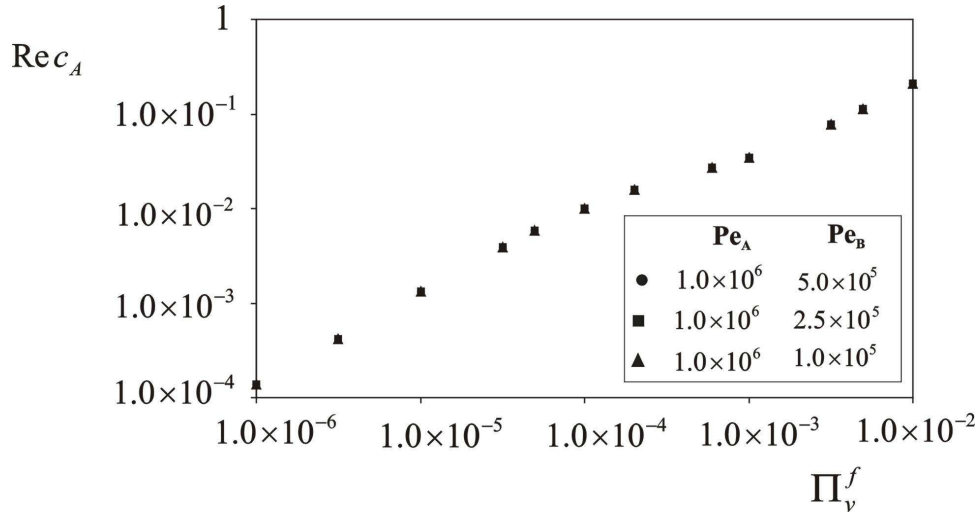


Figure 2.13 - Recovery of component A as a function of Π_v^f

($p_{A/B}^{in} = 50\%$, $n = 8$, $l_m = 100$, $\varepsilon = 0.1$, $\Pi_v^s = 10^{-4}$, $\Pi_{\pi_0}^A = 0$ and $\Pi_{\pi_0}^B = 0$).

2.4.5. Influence of the number of membrane sections

In Figure 2.14, the purity of the solute with the lowest diffusivity is represented for 8 sections. This purity increases along the semi-permeable sub-sections and decreases along the fully-permeable sub-sections. This shows that to optimize the purity it is necessary to use long semi-permeable sections and short fully permeable sections. However, such an approach would contribute to reducing the recovery of the desired component. Another approach, which allows optimization of the purity without reducing the recovery, is the redistribution of the fully permeable area by a different number of sections (keeping the fraction of fully permeable area and the total length). This approach required study of the influence of the number of sections on the purity.

As the number of sections increases, the fraction of the concentrate that comes from the higher regions of the boundary layer decreases and consequently the purity of the concentrate stream increases. The highest purity is for $n = \infty$. This purity was used as a term of comparison for the representation of Figure 2.15, where, $\bar{p}_{A/B}^f / \bar{p}_{A/B}^{-\infty}$ is represented as a function of the number of sections.

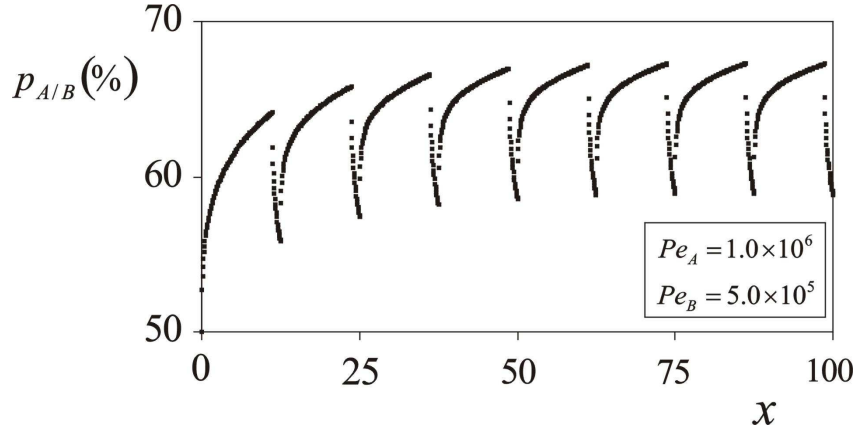


Figure 2.14 - Purity of the solute with the lowest diffusivity (A) along the membrane surface ($p_{A/B}^{in} = 50\%$, $n = 8$, $l_m = 100$, $\varepsilon = 0.1$, $\Pi_v^s = 10^{-4}$, $\Pi_v^f = 10^{-4}$, $\Pi_{\pi_0}^A = 0$, $\Pi_{\pi_0}^B = 0$, $Pe_A = 10^6$, $Pe_B = 5 \times 10^5$).

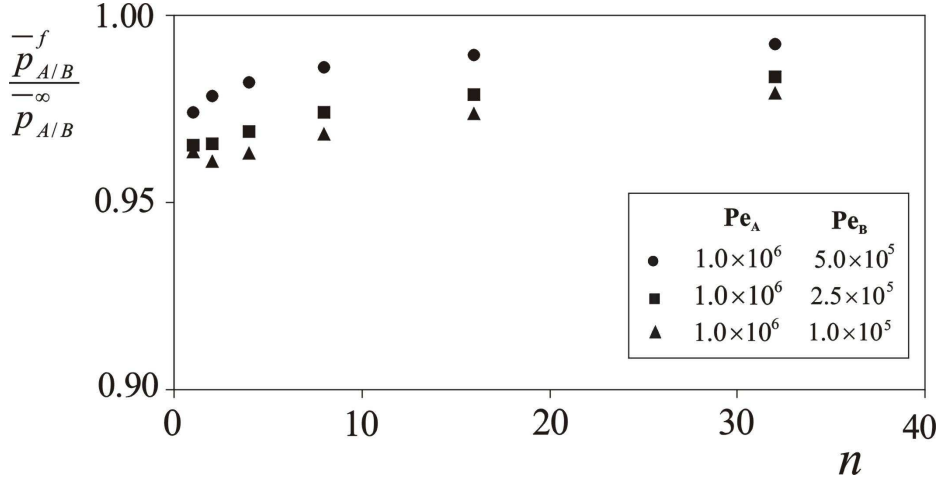


Figure 2.15 – Mean purity of the solute with the lowest diffusivity (A) as a function of the number of sections ($p_{A/B}^{in} = 50\%$, $l_m = 100$, $\varepsilon = 0.1$, $\Pi_v^s = 10^{-4}$, $\Pi_v^f = 10^{-4}$, $\Pi_{\pi_0}^A = 0$, $\Pi_{\pi_0}^B = 0$).

2.5. Conclusions

A new membrane fractionation process based on the combination of hybrid membrane cells and differential diffusion of two solutes was studied by numerical methods. The high purity of the solute with the lower diffusivity in the concentrate stream and the important recovery of the same solute in a compact cell show the potential of this new process. The purity and the recovery of the solute with the lower diffusivity depend on several operational parameters. The effects of the solvent velocity, concentrate velocity and number of sections were studied. The purity increases with the solvent stream velocity but it decreases with the

concentrate stream velocity. The purity increases slightly with the number of sections. The recovery increases with the solvent stream velocity and also with the concentrate stream velocity. The redistribution of the fully permeable area by a different number of sections (keeping the fraction of fully-permeable area and the total length) allows the increase of both purity and recovery. This new fractionation process needs to be further studied particularly the effect of the osmotic pressure of both solutes and the effect of the concentration on the physical properties (viscosity and molecular diffusivity).

2.6. Nomenclature

C	Solute concentration
$\bar{C}$	Normalized solute concentration
C^{in}	Solute concentration at the feed stream
C_m	Solute concentration at the membrane surface
c_m	Normalized solute concentration at the membrane surface
C_p	Permeate solute concentration
c_p	Normalized permeate solute concentration
C_A^f	Solute concentration of A in the concentrate stream
C_B^f	Solute concentration of B in the concentrate stream
C_A^s	Solute concentration of A at the surface of the semi-permeable sub-sections
C_B^s	Solute concentration of B at the surface of the semi-permeable sub-sections
$\left(\overline{C_A^f}\right)_i$	Mean solute concentration of A in the concentrate stream for section i
$\left(\overline{C_B^f}\right)_i$	Mean solute concentration of B in the concentrate stream for section i
$\overline{C_A^f}$	Mean solute concentrations of A in the concentrate stream for the entire cell
$\overline{C_B^f}$	Mean solute concentration of B in the concentrate stream for the entire cell
$\left(\overline{C_A^f}\right)_{ref}$	Mean solute concentration of A in the concentrate stream for the entire cell and for the densest grid

$\left(\overline{C_A^s}\right)_i$	Mean solute concentration of A at the surface of the semi-permeable membrane of section i
$\left(\overline{C_B^s}\right)_i$	Mean solute concentrations of B at the surface of the semi-permeable membrane of section i
$\left(\overline{C_A^s}\right)_m$	Mean solute concentration of A at the surface of all semi-permeable membranes
$\left(\overline{C_B^s}\right)_m$	Mean solute concentration of B at the surface of all semi-permeable membranes
D	Molecular diffusivity
H	Distance between parallel plates
k	Current time step
k_A	First virial coefficient for component A
k_B	First virial coefficient for component B
L_{out}	Length of the outlet section
l_{out}	Normalized length of the outlet section
L_{in}	Length of the inlet section
l_{in}	Normalized length of the inlet section
L_m	Total length of the membrane sections
l_m	Total normalized length of the membrane sections
L	Length of the cell
L	Normalized length of the cell
L_s	Length of a semi-permeable membrane sub-section
l_s	Normalized length of a semi-permeable membrane sub-section
L_f	Length of a fully permeable membrane sub-section
l_f	Normalized length of a fully permeable membrane sub-section
n	Number of sections
ni_s	Number of longitudinal nodes in the semi-permeable section
ni_f	Number of longitudinal nodes in the fully permeable section
n_j	Number of nodes in the vertical direction
$p_{A/B}$	Purity of A in relation to B
$\left(\overline{p_{A/B}^f}\right)_i$	Mean purity of A for the fully-permeable section i

$\overline{p}_{A/B}^f$	Mean purity of A for all fully-permeable sections in the cell
$\left(\overline{p}_{A/B}^s\right)_i$	Mean purity of A for the semi-permeable section i
$\overline{p}_{A/B}^s$	Mean purity of A for all semi-permeable sections in the cell
$p_{A/B}^s$	Mean purity of A over a semi-permeable membrane
$\overline{p}_{A/B}^\infty$	Mean purity of A for a membrane with a infinite number of sections
$p_{A/B}^{in}$	Purity of the feed stream
R_m	Membrane resistance
Rec_A	Recovery of component A
R_ϕ^A	Residual of the mass transport equation
V_0	Mean feed velocity
V_m	Permeate velocity
v_m	Normalized permeate velocity
$\left(\overline{V}_m^s\right)_i$	Mean velocity of the solvent stream for sub-section i
$\overline{V}_m^s$	Mean velocity of the solvent stream for the entire cell
V_x	Longitudinal component of the velocity
V_z	Vertical component of the velocity
v_x	Normalized longitudinal component of the velocity
v_z	Normalized vertical component of the velocity
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Z	Vertical coordinate
z	Normalized vertical coordinate
W	Width of the cell

Non-dimensional numbers

Sc	Schmidt number
Pe	Peclet number
Π_v	$\Delta P - \Delta\pi_0 / R_m V_0$
Π_{π_0}	$\Pi_{\pi_0} = \Pi_0 / \Delta P_m$

$\Pi_{\pi_0}^A, \Pi_{\pi_0}^B$	Equations 2.27 and 2.28
Π_v^s	Solvent velocity of a non-polarized semi-permeable membrane
Π_v^f	Concentrate velocity
Re	Reynolds number
Sh^{imp}	Sherwood number for an impermeable cell
Sh_{ln}^m	Logarithmic Sherwood number
Sh_A^{ln}	Sherwood number for component A based on the film equation
Sh_B^{ln}	Sherwood number for component B based on the film equation

Greek Symbols

ΔP_m	Static pressure difference across a semi-permeable membrane
ε	Fraction of fully-permeable pores
ε_{CA}^f	Numerical error
ε_{crit}	Numerical error of the concentration on a critical location
π	Osmotic pressure
π_0	Feed osmotic pressure
$\Delta\pi_0$	Osmotic pressure difference across the semi-permeable membrane
ψ	Stream function
ω	Vorticity
ρ	Density
μ	Viscosity
ϕ	$\ln(c)$

2.7. References

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Chapter 3

The effect of variable transport properties in the separation of two macromolecules by differential diffusivity in a hybrid membrane cell – a CFD study

A hybrid membrane cell comprising semi and fully-permeable membrane sections, mounted in series, was employed to study the influence of variable transport properties (diffusivity and viscosity) in the separation of two macromolecules by a differential diffusivity mechanism. Separation pairs of bovine serum albumin (BSA)/dextran-T10 (DT10) and bovine serum albumin (BSA)/lysosyme (LYS) were considered. A numerical code was developed to quantify the effect of variable transport properties in the concentration, permeate velocity and purity of the outgoing streams. The variation of the transport properties with concentration reinforces the accumulation of solutes over the semi-permeable membrane. The separation is more effective, with a higher concentration of BSA in the stream crossing the fully permeable membrane, when the accumulation of BSA is reinforced, comparatively to that of the other solute, and vice-versa. For high concentration polarization at semi-permeable membranes surface, the ratio between concentrations of BSA/DT10 and BSA/LYS is equal to 2.0 and 1.4, respectively. BSA purity in the outgoing stream reaches 60% and 56.5% for BSA/DT10 and BSA/LYS, respectively, comparing to the 50% at the cell inlet. For the same operating conditions, supposing constant transport properties, the differential of purity is 20% lower for BSA/DT10 system and 6% higher for BSA/LYS.

The contents of this chapter were adapted from: S.I.S. Pinto, J.M. Miranda, J.B.L.M. Campos, The effect of variable transport properties in the separation of two macromolecules by differential diffusivity in a hybrid membrane cell – a CFD study, *Separation Science and Technology* (2011) in Press.

3.1. Introduction

Separation processes based on diffusion effects are used to separate components with significant molecular diffusivity differences. There are several processes that take advantage of these effects, namely: Diffusion Separation [1], Thermal Diffusion Separation [2], Brownian Motors [3], Field Flow Fractionation (FFF) [4,5], Flow Field Flow Fractionation (FlFFF) [6,7] and Split-Flow Thin-Cell (SPLITT) [8-11].

The Flow Field Flow Fractionation process (FlFFF) [6,7] takes place in a parallel plate cell with two feed streams. The channel flow stream is in the horizontal direction, i.e. along the cell, and the crossflow stream in the vertical direction, i.e. in the perpendicular direction to the cell plates. The upper plate is fully-permeable to the solutes and to the solvent and the lower plate only permeable to the solvent (semi-permeable membrane surface). The solutes are retained by the semi-permeable plate and are dragged out by the channel flow stream. Those with lower diffusivity remain, preferentially, in the vicinity of the semi-permeable membrane and those with higher diffusivity diffuse, faster, into the bulk. Since the velocity profile is parabolic, high diffusivity components leave, in transient state, the device before the solutes with low diffusivity.

In Split-Flow Thin-Cell Fractionation (SPLITT) [8-11], the feed stream is divided by a splitter into two outflow streams with different compositions. The separation is driven by a gradient or a force field. In SPLITT fractionation based on diffusion mechanisms [10], the solute with higher diffusivity leaves through the upper outflow channel, while the solute with lower diffusivity, which remains concentrate near the lower wall, leaves through the inferior outflow channel. In this process, there is no separation membrane.

Pinto et al. [12] studied the potential of a differential diffusivity separation process in Hybrid Membrane Cells [12, 13], which combines characteristics of SPLITT and FlFFF processes. The cell studied comprises, in series, semi-permeable membranes, permeable to the solvent and impermeable to both solutes, and fully-permeable membranes, permeable to all the components (Figure 3.1). The solutes accumulate along the semi-permeable membranes and leave the cell through the fully-permeable membranes. Since the solute with the lower diffusivity remains near the semi-permeable membrane and the solute with higher

diffusivity diffuses away into the bulk, the stream that leaves the cell through the fully permeable membranes is rich in the component with the lower diffusivity. In a Hybrid Membrane Cell, there is a cross-flow in the vertical direction (as in the FLFFF process) and separation in two outflow streams, each one rich in the respective component (as in the SPLITT process). The purity and recovery, according to the authors, strongly depend on several operational parameters [12].

The study of Pinto et al. [12] was carried to demonstrate the concept of differential diffusivity separation by hybrid membrane cells. The study was focused on the main characteristics of the process and several simplifications were made. The transport properties (diffusivity and viscosity) were considered concentration independent and the osmotic pressure was neglected. However, in the mass boundary layer over the semi-permeable membranes, the physical properties, such as diffusivity [14, 15], viscosity [16, 17] and osmotic pressure [14,18], play an important role in the flow patterns and in the mass transfer mechanisms and their values are dependent on the concentration of the solutes.

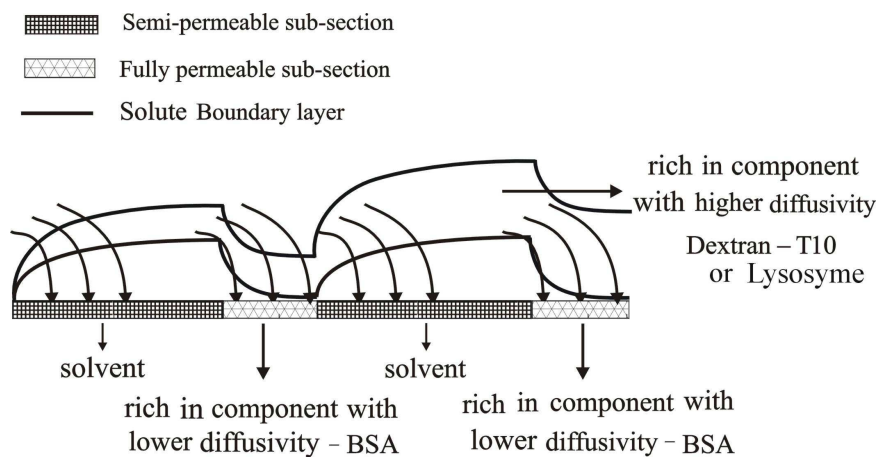


Figure 3.1 – Mass boundary layers for a differential diffusivity process in a Hybrid Membrane Cell.

The molecular diffusivity of a solute decreases with an increase of its concentration in the solution. Therefore, in a binary mixture, the solute with the lower diffusivity accumulates even more over the semi-permeable membrane. On the other hand, the viscosity of the solution increases with an increase of the concentration of the solutes and so it is higher in the vicinity of the semi-permeable membrane than in the bulk. Therefore, the tangential

velocity of the solution decreases with this increase of viscosity, inducing even more accumulation of solutes near the semi-permeable membrane surface.

The permeate velocity also determines the more or less accumulation of a solute at the semi-permeable membrane surface. Following Carman [19], this velocity, V_m , is given by:

$$V_m = \frac{\Delta P_{eff}}{R_m \mu} = \frac{\Delta P - \Delta \pi}{R_m \mu} \quad (3.1)$$

where ΔP_{eff} is the effective pressure, R_m the membrane resistance and μ the viscosity of the fluid. The effective pressure, between concentrate and permeate sides, is equal to the hydrostatic pressure (ΔP) minus the osmotic pressure ($\Delta \pi$). In turn, the osmotic pressure depends on the solute concentration; it is zero when the concentration of the solutes is null and increases when the solute concentration increases. Therefore, if there is any solute in the solution, the effective pressure is lower than the hydrostatic pressure, and, according to eq. 1, the permeate velocity is also lower.

Since the dependence of the physical properties on the concentration influences the mass transport in the vicinity of the semi-permeable membrane, the separation by differential diffusion in a hybrid membrane cell (HMC) is also affected by this dependence. The main objective of this work is to study, and understand, how the variation of these physical properties can determine the separation of macromolecules by a differential diffusivity mechanism in a HMC. This objective is achieved by analysing the separation of bovine serum albumin (BSA) / dextran-T10 (DT10) and the separation of bovine serum albumin (BSA) / lysosyme (LYS).

3.2. Cell description

The hybrid membrane cell under study is schematically represented in Figure 3.2. The cell is divided into three sections: the inlet section (L_{in}), the outlet section (L_{out}) and 4 membrane sections (with total length of L_m). Each membrane section includes a semi-permeable membrane sub-section (L_s) and a fully permeable membrane sub-section (L_f). The semi-permeable membranes are impermeable to the solutes, but permeable to the

solvent, with resistance R_m^s . The fully-permeable membranes are permeable to both solutes and to the solvent, with a permeate velocity equal to v_f . The distance between the walls of the cell is H , the width and length are, W and L , respectively. The width, W , is sufficiently large so that the cell can be considered bi-dimensional. The feed stream is separated into three streams: a retentate stream and two permeate streams. One of the permeate streams crosses the semi-permeable membranes and, since the concentration of the solutes is practically equal to zero, it is called the solvent stream. The other one crosses the fully permeable membranes and, because it is rich in the solute with the lower diffusivity, it is called the concentrate stream. The two permeate streams are collected in two independent permeate chambers: the solvent chamber and the concentrate chamber. The mean velocity of the feed is V_0 .

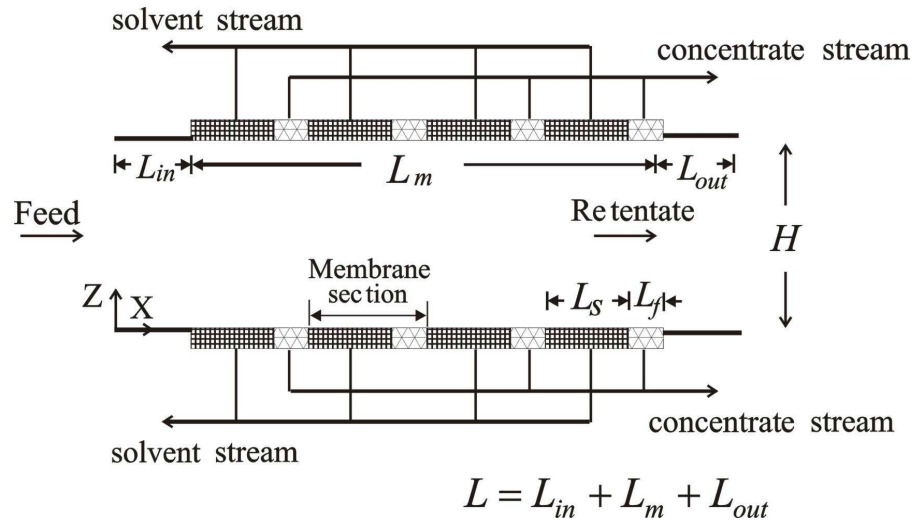


Figure 3.2 - Schematic representation of the hybrid membrane cell.

The type of membrane used in the semi-permeable sub-section and the hybrid membrane cell dimensions, are listed in Table 3.1.

For a better understanding, along the text, all the uppercase variables symbolize dimensional variables and the lowercase normalised variables. The concentrations are normalized by the inlet concentration of the solutes, C_{BSA}^{in} , C_{DT10}^{in} and C_{LYS}^{in} , the velocities by the inlet velocity and the geometric dimensions by the height of the cell.

Table 3.1 - Characteristics of the Hybrid Membrane Cell.

Membrane	OMEGA Polysulfone membrane
R_m^s	$5.714 \times 10^{12} \text{ m}^{-1}$
H	0.001 m
L_m	0.5556 m
L_s	0.125 m
L_f	0.0139 m
$L_{in} = L_{out}$	0.04 m

3.3. Physical properties

The two feed stream studied are aqueous solutions with dissolved molecules of Bovine Serum Albumin (BSA) / Dextran-T10 or BSA / Lysosyme with pH = 4.7 and ionic strength of 0.15 M which corresponds to the BSA isoelectric point. The molecular weight of BSA is 69 000 Da, the molecular weight of Dextran-T10 and Lysosyme are 10 000 Da and 14 600 Da, respectively. Care was taken on choosing, in the literature, correlations of physical properties (diffusivity, viscosity and osmotic pressure) for the operating values of pH and ionic strength. The diffusivity of Dextrans with low molecular weights (Dextran-T10) is almost constant from diluted solutions until concentrations around 100 kg/m^3 [20] and so a constant value, $10.5 \times 10^{-11} \text{ m}^2/\text{s}$ [15, 21] was used.

The viscosity of the mixture of BSA/DT10 or BSA/LYS, $\bar{\mu}$, was calculated by:

$$\bar{\mu} = \mu_i x_i + \mu_j x_j \quad (3.2)$$

where x_i and x_j are the mass fractions of the macromolecules to be separated, and μ_i and μ_j the viscosity of the respective pure components; i refers to BSA and j refers to DT10 or LYS.

The osmotic pressure of each component, BSA, DT10 and LYS, is non-linearly dependent on the respective concentration:

$$\pi_i = k_1^i C_i + k_2^i C_i^2 + k_3^i C_i^3 \quad (3.3)$$

The values k_1^i , k_2^i and k_3^i were obtained from Leung and Probstein [14] for BSA, from Jonsson [18] for Dextran-T10 and from Moon et al. [22] for Lysosyme. The viscosity, diffusivity and osmotic pressure of each solute, for a solution with pH = 4.7 and an ionic force of 0.15 M, are listed in Table 3.2.

Table 3.2 – Viscosity, diffusivity and osmotic pressure of BSA, Dextran-T10 and Lysosyme.

<i>Equations</i>			
<i>Property</i>	BSA	Dextran-T10	Lysosyme
Viscosity [Pa.s]	$\mu = 9.086 \times 10^{-4} \times e^{2.44 \times 10^{-5} C^2}$ Gill et al. [16]	$\mu = 10^{-3} + 1.85 \times 10^{-5} C - 5.0 \times 10^{-8} C^2 + 6.67 \times 10^{-10} C^3$ Field and Aimar [17]	$\mu = 1 \times 10^{-3} \exp\left(\frac{2.718 \times 10^{-3} C}{1 - 1.843 \times 10^{-3} C}\right)$ Monkos [23]
Diffusivity [m ² /s]	$D = (7 - 0.0041C) \times 10^{-11}$ Leung and Probstein [14]	$D = 10.5 \times 10^{-11}$ De and Bhattacharya [15]	$D = (1.225 - 0.0038C) \times 10^{-10}$ Prince et al. [24]
Osmotic pressure	$\pi = 2.3 \times 10^2 C - 1.34 C^2 + 3.09 \times 10^{-3} C^3$ Leung and Probstein [14]	$\pi = 1.116 \times 10^3 C - 4.91 C^2 + 2.57 \times 10^{-2} C^3$ Jonsson [18]	$\pi = 1.438 \times 10^2 C + 0.336 C^2 - 1.53 \times 10^{-2} C^3$ Moon et al. [22]

3.4. Numerical method

The flow and mass transport in the cell were studied by numerical methods. The conservative equations and boundary conditions were discretized and the solution of the discretized equations implemented in a numerical code. The discretization was done by the finite differences method. The main outputs of the numerical code are the flow and concentration fields. The structure of the code is similar to that employed by Afonso et al. [25] to study the effect of the physical properties in the purification of BSA in a conventional cell (parallel plate cell). The conclusions, in a conventional cell, were validated by

experimental data from literature. This validation is important to support the conclusions of the present study, since the manufacture of hybrid membrane cells is yet under development.

3.4.1. Domain

The conservative equations were solved for the domain represented in Figure 3.3. The domain corresponds to half of the cell (the cell is symmetric) and has an inlet section, an outlet section and 4 membrane sections, each with two sub-sections. The fully permeable sub-sections are usually shorter than the semi-permeable ones. The domain was discretized and converted into a grid of discrete nodes.

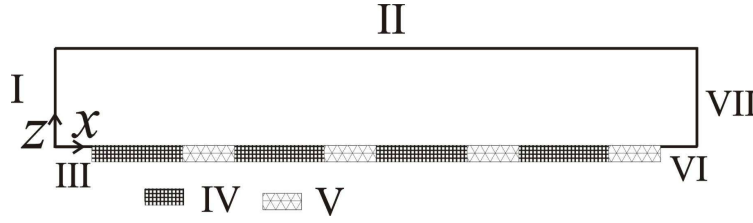


Figure 3.3 – Schematic representation of the domain (cell with four membrane sections) and respective boundaries (I – cell inlet; II – symmetric axis; III – wall; IV – semi-permeable membrane; V – fully-permeable membrane; VI – wall; VII – cell outlet).

3.4.2. Equations

The flow in the cell is described by the Navier-Stokes equations. For a bi-dimensional cell, the dimensionless Navier-Stokes equations can be written for secondary variables (vorticity, ω , and stream function, ψ) and Cartesian coordinates (x and z). Considering a multicomponent incompressible flow and variable viscosity, the flow equations, in their velocity formulation, are:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0 \quad (3.4)$$

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_x}{\partial z} = -Eu_0 \frac{\partial p}{\partial x} + \left[\frac{\partial \left(2 \frac{1}{Re} \frac{\partial v_x}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{1}{Re} \frac{\partial v_z}{\partial x} + \frac{1}{Re} \frac{\partial v_x}{\partial z} \right)}{\partial z} \right] \quad (3.5)$$

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_z \frac{\partial v_z}{\partial z} = -Eu_0 \frac{\partial p}{\partial x} + \left[\frac{\partial \left(2 \frac{1}{\text{Re}} \frac{\partial v_z}{\partial z} \right)}{\partial z} + \frac{\partial \left(\frac{1}{\text{Re}} \frac{\partial v_z}{\partial x} + \frac{1}{\text{Re}} \frac{\partial v_x}{\partial z} \right)}{\partial x} \right] \quad (3.6)$$

In these equations, x represents the normalized longitudinal coordinate, z the normalized transversal coordinate. The Reynolds number, Re , is based on the distance between plates, H , mean inlet velocity, V_0 and mean solution viscosity, $\bar{\mu}$:

$$\text{Re} = \frac{\rho V_0 H}{\mu} \quad (3.7)$$

where ρ is the fluid density.

Equations (3.4), (3.5) and (3.6) can be written in a stream function-vorticity formulation:

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} \quad (3.8)$$

$$\frac{\partial \omega}{\partial t} + \left(v_x - 2 \frac{\partial}{\partial x} \frac{1}{\text{Re}} \right) \frac{\partial \omega}{\partial x} + \left(v_z - 2 \frac{\partial}{\partial z} \frac{1}{\text{Re}} \right) \frac{\partial \omega}{\partial z} = \omega \left(\frac{\partial^2}{\partial x^2} \frac{1}{\text{Re}} + \frac{\partial^2}{\partial z^2} \frac{1}{\text{Re}} \right) + \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial z^2} \right) + S \quad (3.9)$$

where S is:

$$S = -2 \left(\frac{\partial^2}{\partial x^2} \frac{1}{\text{Re}} \frac{\partial^2 \psi}{\partial z^2} - 2 \frac{\partial^2}{\partial x \partial z} \frac{1}{\text{Re}} \frac{\partial^2 \psi}{\partial x \partial z} + \frac{\partial^2}{\partial z^2} \frac{1}{\text{Re}} \frac{\partial^2 \psi}{\partial x^2} \right) \quad (3.10)$$

Equation (3.8) is a Poisson-type equation and equation (3.9) is the vorticity transport equation for variable viscosity.

The dimensionless stream function ψ is defined by:

$$v_x = \frac{\partial \psi}{\partial z} \quad (3.11)$$

$$v_z = -\frac{\partial \psi}{\partial x} \quad (3.12)$$

The dimensionless mass transport equation in Cartesian coordinates for each solute, i (BSA) and j (DT10 or LYS), in a binary mixture with variable diffusivities is:

$$\frac{\partial c_i}{\partial t} + v_x \frac{\partial c_i}{\partial x} + v_z \frac{\partial c_i}{\partial z} = \frac{\partial \left(\frac{1}{Pe_i} \frac{\partial c_i}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{1}{Pe_i} \frac{\partial c_i}{\partial z} \right)}{\partial z} \quad (3.13)$$

$$\frac{\partial c_j}{\partial t} + v_x \frac{\partial c_j}{\partial x} + v_z \frac{\partial c_j}{\partial z} = \frac{\partial \left(\frac{1}{Pe_j} \frac{\partial c_j}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{1}{Pe_j} \frac{\partial c_j}{\partial z} \right)}{\partial z} \quad (3.14)$$

The Peclet numbers, Pe_i and Pe_j , are defined by:

$$Pe_i = \frac{V_0 H}{D_i} \quad (3.15)$$

$$Pe_j = \frac{V_0 H}{D_j} \quad (3.16)$$

In these equations, D_i and D_j represent the molecular diffusivity of i (BSA) and j (DT10 or LYS) in the solution, respectively.

If a variable ϕ is defined by

$$\phi = \ln c \quad (3.17)$$

the mass transport equations are transformed into the so-called ϕ equations which were solved by the so-called ϕ method [26].

$$\frac{\partial \phi_i}{\partial t} + \left(v_x - \frac{\partial}{\partial x} \frac{1}{Pe_i} - \frac{1}{Pe_i} \frac{\partial \phi_i}{\partial x} \right) \frac{\partial \phi_i}{\partial x} + \left(v_z - \frac{\partial}{\partial z} \frac{1}{Pe_i} - \frac{1}{Pe_i} \frac{\partial \phi_i}{\partial z} \right) \frac{\partial \phi_i}{\partial z} = \frac{1}{Pe_i} \left(\frac{\partial^2 \phi_i}{\partial x^2} + \frac{\partial^2 \phi_i}{\partial z^2} \right) \quad (3.18)$$

$$\frac{\partial \phi_j}{\partial t} + \left(v_x - \frac{\partial}{\partial x} \frac{1}{Pe_j} - \frac{1}{Pe_j} \frac{\partial \phi_j}{\partial x} \right) \frac{\partial \phi_j}{\partial x} + \left(v_z - \frac{\partial}{\partial z} \frac{1}{Pe_j} - \frac{1}{Pe_j} \frac{\partial \phi_j}{\partial z} \right) \frac{\partial \phi_j}{\partial z} = \frac{1}{Pe_j} \left(\frac{\partial^2 \phi_j}{\partial x^2} + \frac{\partial^2 \phi_j}{\partial z^2} \right) \quad (3.19)$$

In the ϕ method, the transformation $\phi = \ln(c)$ is used to linearize the concentration gradients in the mass boundary layer over the membrane, improving the accuracy of the solution for a given grid.

The equations were discretized by a general procedure described in Afonso et al. [25]. The mass transport equations were solved implicitly and the vorticity transport equation by a semi-implicit method. The convection, diffusion and independent terms were solved implicitly and the source term explicitly. A hybrid method combining upwind and central differences discretization, according to the local Peclet number, was used for the convective terms of both equations.

3.4.3. Boundary conditions

Boundary conditions I, II, III, VI and VII (Figure 3.3) are given by Miranda and Campos [13]. The boundary conditions for the semi-permeable membrane (boundary IV) are also analyzed by Miranda and Campos [13], but the velocity, in this boundary, depends on the osmotic pressure difference across the semi-permeable membrane ($\Delta\pi_{i/j}$) which, in turn, depends on the concentrations of the binary mixture. This boundary condition is going to be briefly discussed in conjunction with the boundary conditions for the fully permeable membranes (boundaries V).

The permeate velocity, normal velocity component, at the semi-permeable membranes can be expressed by the ratio between the flow driving force and the resistance to the flow [27]:

$$-v_z = \frac{\Delta P - \Delta\pi_{i/j}}{\bar{\mu}_p^s R_m^s V_0} = \frac{\Delta P - (\pi_i^m + \pi_j^m)}{\bar{\mu}_p^s R_m^s V_0} \quad \text{at } z = 0 \quad (3.20)$$

where ΔP , π_i^m and π_j^m represent the applied pressure difference and the osmotic pressure of component i (BSA) and component j (DT10 or LYS), respectively, at the semi-permeable membrane surface, R_m^s the permeation resistance of the semi-permeable membrane and $\bar{\mu}_p^s$ the respective viscosity of the permeate flux.

The non-linear dependence between osmotic pressure and concentration of the solutes at the semi-permeable membrane surface is given by:

$$\pi_i^m = k_1^i C_i^{in} c_i + k_2^i (C_i^{in})^2 c_i^2 + k_3^i (C_i^{in})^3 c_i^3 \quad (3.21)$$

$$\pi_j^m = k_1^j C_j^{in} c_j + k_2^j (C_j^{in})^2 c_j^2 + k_3^j (C_j^{in})^3 c_j^3 \quad (3.22)$$

Combining the previous equations, the velocity boundary condition is given by:

$$-v_z = \frac{\Pi_v}{1 - (\Pi_{\pi_0}^i)_1 - (\Pi_{\pi_0}^j)_1} \left[1 - (\Pi_{\pi_0}^i)_1 c_i - (\Pi_{\pi_0}^j)_1 c_j - \frac{k_2^i (C_i^{in})^2}{k_1^i C_i^{in}} (\Pi_{\pi_0}^i)_2 c_i^2 - \frac{k_2^j (C_j^{in})^2}{k_1^j C_j^{in}} (\Pi_{\pi_0}^j)_2 c_j^2 + \right. \\ \left. - \frac{k_3^i (C_i^{in})^3}{k_1^i C_i^{in}} (\Pi_{\pi_0}^i)_3 c_i^3 - \frac{k_3^j (C_j^{in})^3}{k_1^j C_j^{in}} (\Pi_{\pi_0}^j)_3 c_j^3 \right] \quad (3.23)$$

where the non-dimensional numbers are defined by:

$$\Pi_v = \frac{\Delta P - k_1^i C_i^{in} - k_1^j C_j^{in}}{\bar{\mu}_p^s R_m^s V_0} \quad (3.24)$$

$$(\Pi_{\pi_0}^i)_1 = \frac{k_1^i C_i^{in}}{\Delta P}; (\Pi_{\pi_0}^i)_2 = \frac{k_2^i C_i^{in}}{\Delta P}; (\Pi_{\pi_0}^i)_3 = \frac{k_3^i C_i^{in}}{\Delta P} \quad (3.25)$$

$$(\Pi_{\pi_0}^j)_1 = \frac{k_1^j C_j^{in}}{\Delta P}; (\Pi_{\pi_0}^j)_2 = \frac{k_2^j C_j^{in}}{\Delta P}; (\Pi_{\pi_0}^j)_3 = \frac{k_3^j C_j^{in}}{\Delta P} \quad (3.26)$$

The values of k_1^i , k_2^i and k_3^i for BSA and k_1^j , k_2^j and k_3^j for DT10 or LYS are given in Table 3.2.

The physical meaning of the non-dimensional groups cited above is described in detail by Miranda and Campos [28].

For the fully-permeable sub-sections, the osmotic pressure difference across the membrane is zero and so the permeate velocity is given by:

$$v_f = \frac{\Delta P^f}{\bar{\mu}_p^f R_m^f V_0} \quad (3.27)$$

where the superscript f indicates that the variables are for a fully-permeable sub-section.

At the semi-permeable membranes, $z = 0$, and for each component, the normal convective flux promoted by suction is equal to the diffusive flux, in the opposite direction, promoted by the concentration gradient between the semi-permeable membrane surface and the bulk:

$$-\frac{1}{\text{Pe}_i} \frac{\partial c_i}{\partial z} = v_s c_i^{m,s} \quad (3.28)$$

where $c_i^{m,s}$ is the normalized solute concentration at the semi-permeable membrane surface.

For the fully-permeable membrane, the diffusive flux is equal to zero:

$$\frac{1}{\text{Pe}_i} \frac{\partial c_i}{\partial z} = 0 \quad (3.29)$$

In an outflow stream, the concentration gradient is mainly due to convective effects and so, the diffusive effect can be considered negligible.

All the boundaries conditions, for semi-permeable (boundary IV) and fully permeable membranes (boundary V), are given in Table 3.3.

Table 3.3 - Semi-permeable and fully-permeable membrane boundary conditions.

IV	V
$v_x = 0$	$v_x = 0$
Equation 3.23	Equation 3.27
$\psi = \frac{11}{16} + \int -v_z dx$	$\psi = \frac{11}{16} + \int -v_z dx$
$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$	$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$
Equation 3.28	Equation 3.29
$-\frac{\partial \phi_i}{\partial z} = 1$	$\frac{\partial \phi_i}{\partial z} = 0$

3.5. Grid tests

The accuracy of the grid used to solve the discretized equations was studied by performing several grid tests following the methodology of previous works [12, 13]. Grid tests were performed for variable properties, high feed concentrations, the highest transmembrane pressure and the lowest permeate velocity at the fully permeable subsections, i.e., for high concentration polarization conditions at the semi-permeable subsections. The discretization error was the independent parameter chosen to quantify these tests and to choose the accurate grid:

$$\mathcal{E}_{c_i}^{-m,s} = \frac{\left(\overline{c_i}^{-m,s} \right)_{ref} - \overline{c_i}^{-m,s}}{\left(\overline{c_i}^{-m,s} \right)_{ref}} \quad (3.30)$$

where $\overline{c_i}^{-m,s}$ refers to the mean normalized concentration of component i at the semi-permeable membrane surface, integrated along the total length of the semi-permeable subsections, and is defined by:

$$\frac{c_i^{-m,s}}{c_i} = \frac{\int_0^{n \times l_s} c_i^{m,s} dx}{\int_0^{n \times l_s} dx} \quad (3.31)$$

The index *ref* refers to the grid reference. The results of the grid tests for the separation of BSA and DT10 (as example) are summarized in Table 3.4.

Table 3.4 – Grid tests ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $\text{Re}_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $\text{Pe}_{BSA}^0 = 2.37 \times 10^7$; $\text{Pe}_{DT10}^0 = 1.55 \times 10^7$; $\nu_f = 1 \times 10^{-6}$; $\Delta P = 2.43 \times 10^5 \text{ Pa}$; $n = 4$; $l_m = 500$).

<i>Grid</i>	ni_m [a]	$\mathcal{E}_{C_{BSA}}^{-m,s}$	$\mathcal{E}_{C_{DT10}}^{-m,s}$
(n × m)			
Normal direction			
497 × 251	480	1.67%	0.21%
497 × 501	480	0.80%	0.14%
497 × 1001	480	ref. grid	ref. grid
Tangential direction			
257 × 501	240	1.86%	0.63%
497 × 501	480	0.56%	0.19%
977 × 501	960	ref. grid	ref. grid

[a] ni_m is the number of grid nodes at the membrane surface

The discretization error of BSA is the highest, since this component is the most concentrated in the vicinity of the semi-permeable membrane. The results show that a grid of 497×501 is sufficient to obtain a discretization error less than 1% (both components) in the normal and tangential directions (Table 3.4). This grid, 497×501, was used for all simulations.

3.6. Convergence

The convergence of the numerical method was checked through the sum of the residues of the vorticity and mass transport equations of both components ($R_t = R_\omega + R_{c_{DT10}^m} + R_{c_{BSA}^m}$)

and also by analysing the evolution of the difference (ϵ_{crit}), in two consecutive iterations, between the values of the concentration, in a critical point of the cell located near the end of the last semi-permeable membrane sub-section.

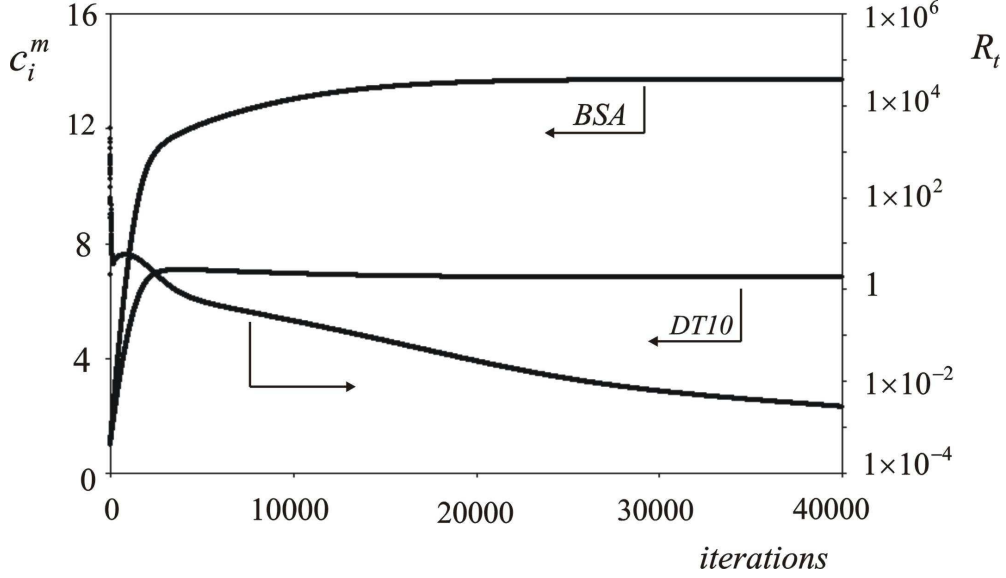


Figure 3.4 – Evolution of the normalized concentration of both components in a critical node and total residues of the vorticity and mass transport equations as a function of the number of iterations

$$(C_{BSA}^{in} = 24.4 \text{ kg/m}^3; C_{DT10}^{in} = 24.4 \text{ kg/m}^3; \text{Re}_0 = 1387; V_0 = 1.632 \text{ m/s}; \text{Pe}_{BSA}^0 = 2.37 \times 10^7; \\ \text{Pe}_{DT10}^0 = 1.55 \times 10^7; \nu_f = 1 \times 10^{-6}; \Delta P = 2.43 \times 10^5 \text{ Pa}; n = 4; l_m = 500).$$

The evolution of these parameters for the separation of BSA and DT10 (as example) is represented in Figure 3.4 for severe, in terms of convergence, operating conditions. The data of Figure 3.4 show that the concentrations of the components converge to a constant value, and, at the same time, the sum of the residues decrease until a very small value, $R_t < 10^{-2}$. Based on these and on previous results, the following convergence criterion was adopted:

$$\left\{ \begin{array}{l} \epsilon_{crit} < 10^{-3} \\ R_t < 10^{-2} \end{array} \right. \quad (3.32)$$

3.7. Results and discussion

Numerical data were obtained for the separation of two macromolecules (i and j) in a Hybrid Membrane Cell by differential diffusion of both components. Two separation pairs of

macromolecules were studied: BSA (i) / DT10 (j) and BSA (i) / LYS (j). BSA is the component with the lowest diffusivity in these two pairs of macromolecules.

Data for:

- case 1: variable transport properties (diffusivity and viscosity) and non-linear relation of the osmotic pressure ($\Delta\pi_{i/j}$) with the concentration of the components;
- case 2: constant transport properties (diffusivity and viscosity) and non-linear relation of the osmotic pressure ($\Delta\pi_{i/j}$) with the concentration of the components;

are presented, in order to show the effect of the variable transport properties on the concentration of the solutes at the semi-permeable membrane surface and on the purity of the concentrate stream.

Moreover, data for:

- case 3: variable transport properties (diffusivity and viscosity) and negligible osmotic pressure ($\Delta\pi_{i/j}$) of the components;

are presented to study the effect of the osmotic pressure on the velocity and on the concentration of the solutes at the semi-permeable membrane surface.

For these three cases, the velocity of the solvent stream is calculated by equation (3.20) using the viscosity of the water (solvent). The concentrate velocity will be taken constant and will be evaluated by equation (3.27) with the viscosity of the feed stream. Results for a variable concentrate velocity, evaluated at local viscosity, will be presented in a separated section (section 3.7.3.3).

3.7.1. Ratio between concentrations at semi-permeable membrane surface

The objective of this section is to analyze mean data for low and high concentration polarization at the semi-permeable membrane surface for the separation of two pairs of macromolecules: BSA / DT10 (Figure 3.5a) and BSA / LYS (Figure 3.5b).

Figure 3.5a and 3.5b represent the ratio between the mean concentrations, BSA/DT10 and BSA/LYS, respectively, at the semi-permeable membrane surface as a function of the applied transmembrane pressure.

For very low transmembrane pressures, in both systems, low concentration polarization at the semi-permeable membrane surface is observed. The concentration of BSA at the surface tends to be equal to that of Dextran-T10 (Figure 3.5a) or to that of Lysosyme (Figure

3.5b), independently of the permeate velocity through the fully-permeable sub-sections, i.e., there is no separation by diffusivity difference of the solutes. The concentration ratio increases with increasing transmembrane pressure.

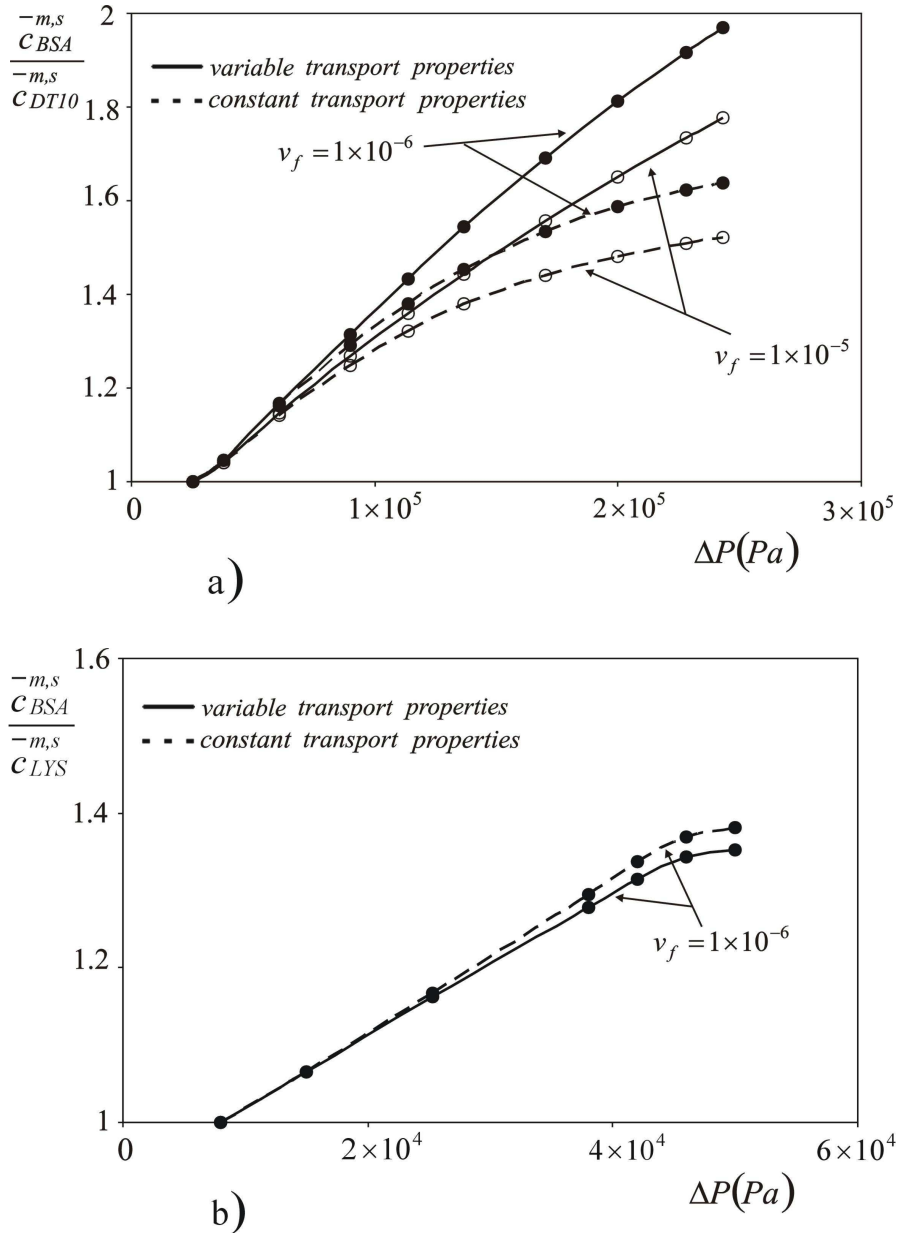


Figure 3.5 – Ratio between the mean normalized concentrations at the semi-permeable membrane surface as a function of the transmembrane pressure a) BSA/Dextran-T10 system ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $Pe_{BSA}^0 = 2.37 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$; $n = 4$); b) BSA/Lysosyme system ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{LYS}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1404$; $V_0 = 1.400 \text{ m/s}$; $Pe_{BSA}^0 = 2.03 \times 10^7$; $Pe_{LYS}^0 = 1.24 \times 10^7$; $n = 4$).

For the separation of BSA/DT10 and high levels of concentration polarization (high applied pressure difference – 2.5×10^5 Pa), the concentration ratio at the semi-permeable membrane surface supposing variable transport properties is higher than that supposing constant properties (Figure 3.5a). This ratio is 2.0 and 1.8 (case 1), for normalized permeate velocities at the fully-permeable membranes, v_f , equal to 1×10^{-6} and 1×10^{-5} , respectively. This ratio increases with the decrease of the permeate velocity through the fully permeable sub-sections. Supposing constant transport properties (case 2), the same ratio is 22% and 18% lower, respectively. Then, for high inlet concentration of the components, there is an improvement of the fractionation process due to the effect of variable transport properties.

For the separation of BSA/LYS, the accumulation of solutes at the semi-permeable membranes surface is very high. Consequently, a low range (comparatively to the previous separation) of transmembrane pressure (Figure 3.5b) is sufficient to achieve high levels of concentration polarization.

In opposition to BSA/DT10, the concentrations ratio of BSA/LYS, supposing variable transport properties, is lower than that obtained supposing constant transport properties (Figure 3.5b). The LYS diffusivity is lower than that of DT10 and its variation with concentration induces a higher increase of LYS (in percentage) at the semi-permeable membrane surface than that of BSA. For this reason, the concentrations ratio at the semi-permeable membrane surface is 2.2% lower when variable transport properties are considered.

3.7.2. Purity of BSA

The purity of BSA (Figures 3.6a and 3.6b) in the outflow streams through the fully-permeable sub-sections is defined by:

$$Pu_{BSA}(\%) = \frac{C_{BSA}^{m,f}}{C_{BSA}^{m,f} + C_j^{m,f}} \quad (3.33)$$

where j refers to the component with higher diffusivity: DT10 and LYS, for the separation of BSA / DT10 and BSA / LYS, respectively.

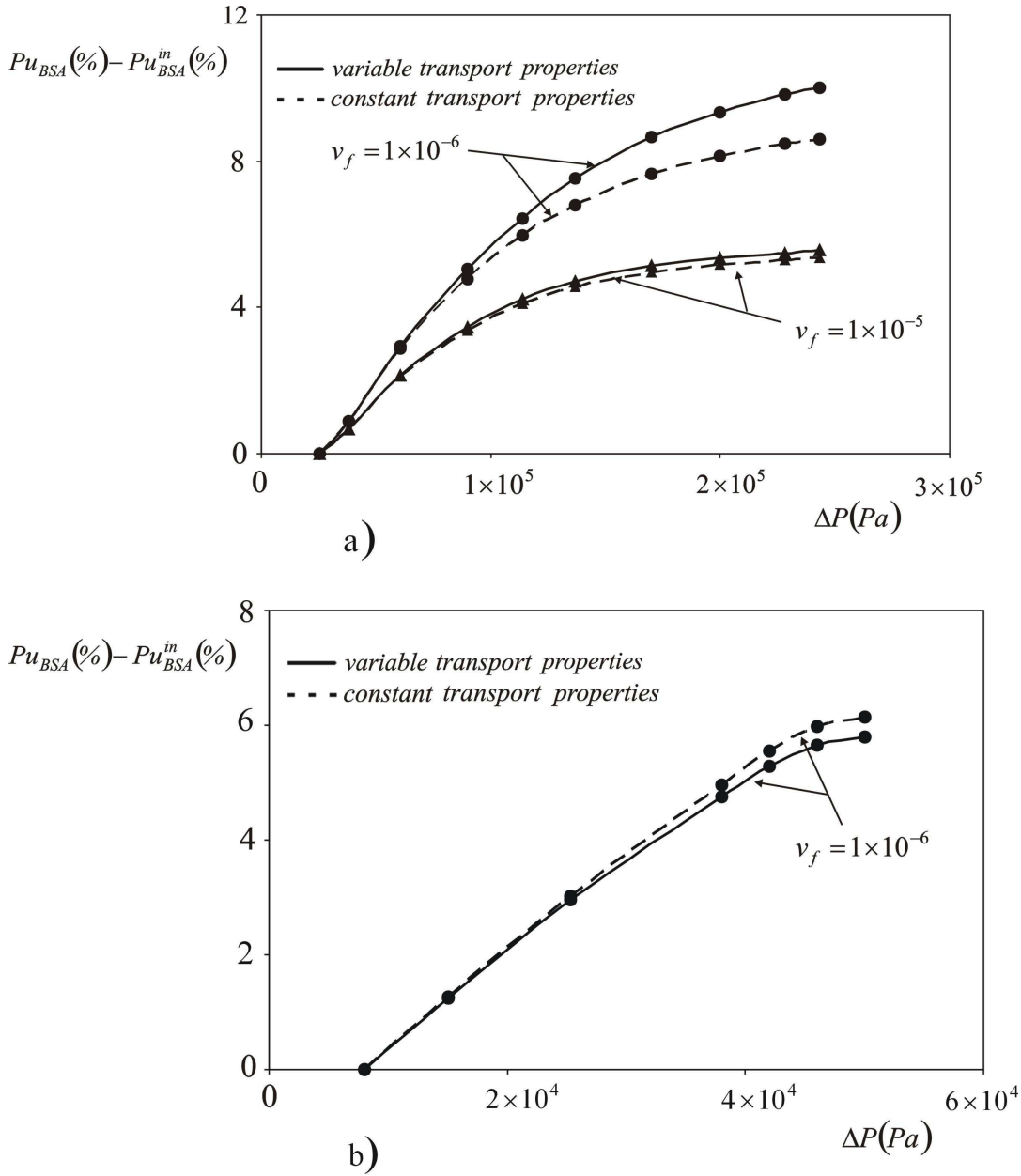


Figure 3.6 – $Pu_{BSA}(\%) - Pu_{BSA}^{in}(\%)$ as a function of the transmembrane pressure a) BSA/Dextran-T10 system ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $Pe_{BSA}^0 = 2.37 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$; $n = 4$); b) BSA/LYS system ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{LYS}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1404$; $V_0 = 1.400 \text{ m/s}$; $Pe_{BSA}^0 = 2.03 \times 10^7$; $Pe_{LYS}^0 = 1.24 \times 10^7$; $n = 4$).

For very low values of the transmembrane pressure through the semi-permeable sub-sections, the purity of BSA is around 50% whatever the permeate velocity through the fully permeable sub-sections, i.e. there is no separation since the feed stream is 50% of BSA and 50% of the other component (Figures 3.6a and 3.6b). As the transmembrane pressure increases, the purity of BSA increases (Figures 3.6a and 3.6b), since more quantity of BSA,

relatively to that of Dextran-T10 or Lysosyme, crosses the fully permeable sub-section due to the BSA accumulation in the adjacent semi-permeable membrane surface (Figures 3.5a and 3.5b).

For the separation BSA/DT10, this increase in the BSA purity is even higher when the effect of the concentration of the solutes in the transport properties is taken into account (Figure 3.6a). This effect is responsible for an increase in the purity of around 20% for a transmembrane pressure 2.5×10^5 Pa and v_f equal to 1×10^{-6} . Moreover, the purity increases with the decrease of the permeate velocity through the fully permeable sub-sections (Figure 3.6a), because more concentrate fluid (in percentage of the total) comes from the adjacent (polarized by concentration) semi-permeable membrane. Therefore, the effect of variable transport properties is even more effective for low values of the permeate velocity through the fully-permeable sub-sections.

For the separation of BSA/LYS, the opposite happens. The BSA purity is lower when variable transport properties are considered (Figure 3.6b). This behaviour is due to the higher increase (in percentage) of lysosyme concentration at the semi-permeable membranes surface. This effect is responsible for a decrease of 6% in the purity, for a transmembrane pressure of 5×10^4 Pa.

3.7.3. Detailed analysis of the separation process of BSA / DT10

In the following sections are analyzed, in detail, the separation process of BSA / DT10 when variable physical properties are considered for high concentration polarization.

3.7.3.1. Concentration and flow fields of the separation of BSA and Dextran-T10

Figure 3.7 is useful to understand the separation process of BSA and DT10. Figures 3.7a and 3.7b show the flow field and the iso-concentration lines of both solutes for a high concentration polarization of the semi-permeable membrane surface and variable transport properties (case 1). Figures 3.7c and 3.7d show the iso-concentration lines for the same conditions, but supposing constant transport properties, diffusivity and viscosity (case 2).

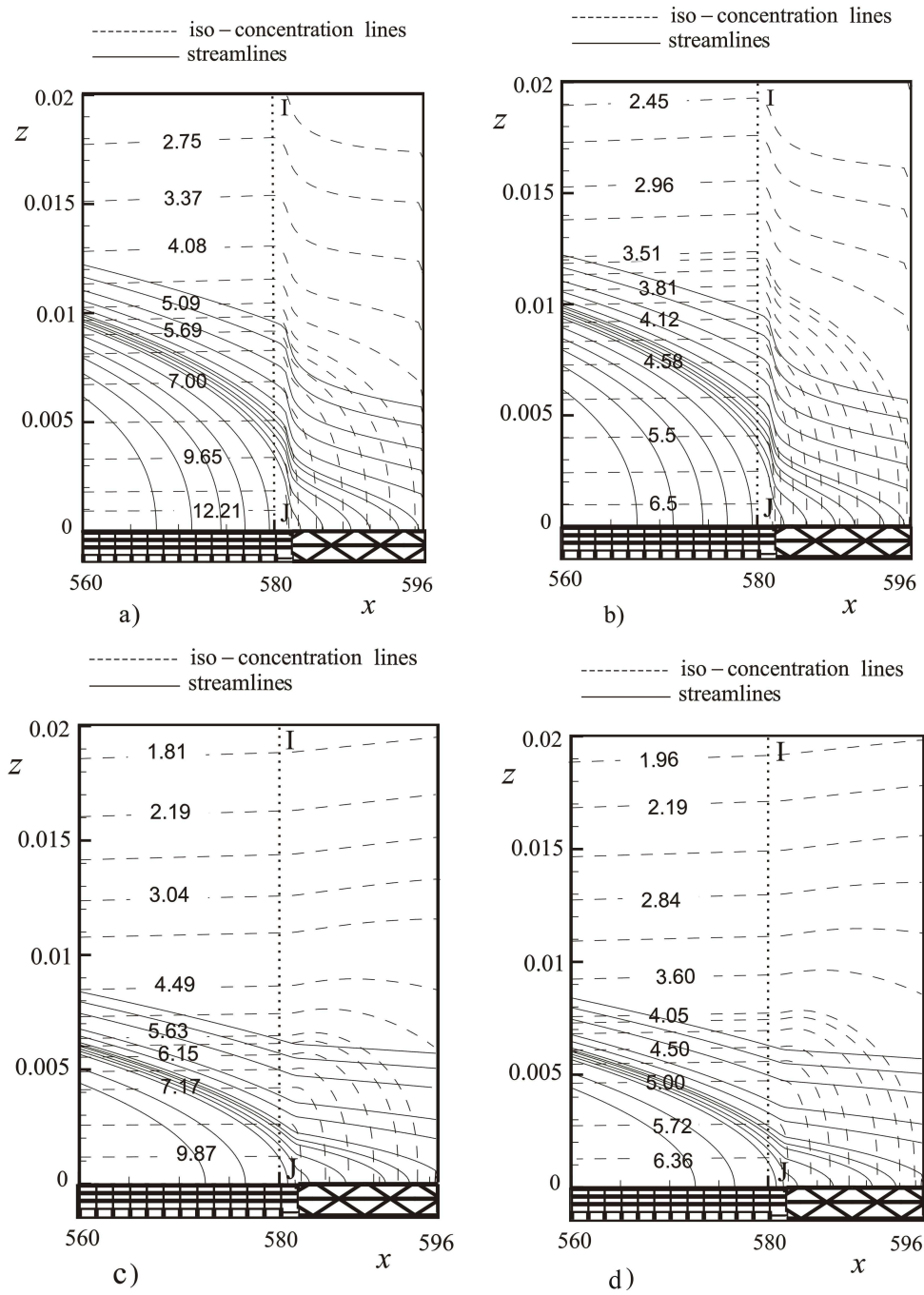


Figure 3.7 – Streamlines and iso-concentration lines in the vicinity of the membrane at the end of the 4th section, a) BSA and supposing variable transport properties – case 1; b) DT10 and supposing variable transport properties – case 1; c) BSA and supposing constant transport properties – case 2; d) DT10 and supposing constant transport properties – case 2 ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $\text{Re}_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $\text{Pe}_{BSA}^0 = 2.37 \times 10^7$; $\text{Pe}_{DT10}^0 = 1.55 \times 10^7$; $v_f = 1 \times 10^{-6}$; $\Delta P = 2.43 \times 10^5 \text{ Pa}$).

BSA is the component with the lowest diffusivity, and so, its concentration is higher in the vicinity of the semi-permeable membrane. The streamlines of the fluid leaving the cell through the fully-permeate sub-section cross this region, rich in BSA and poor in Dextran-T10, and so the outcome is a concentrate stream rich in BSA. For high values of inlet concentrations, the semi-permeable membrane surface concentrations are significantly higher than those in the bulk, in particularly for BSA. This difference is even more accentuated if variable physical properties are considered (case 1).

This difference is, for BSA, manly justified by the diffusivity dependence on concentration [14]: the increase in BSA concentration leads to lower diffusivity and, consequently, to a stronger accumulation near the semi-permeable membrane. This effect is clearly seen comparing Figures 3.7a and 3.7c.

For Dextran-T10 the effect referred above is not so important, since the diffusivity of Dextran-T10 is independent of the concentration [15]. However, comparing cases 1 and 2 - Figures 3.7b and 3.7d -, the concentration of Dextran-T10 at the semi-permeable membrane surface is higher (although slightly) due to the effect of variable Reynolds number (see Figure 3.8).

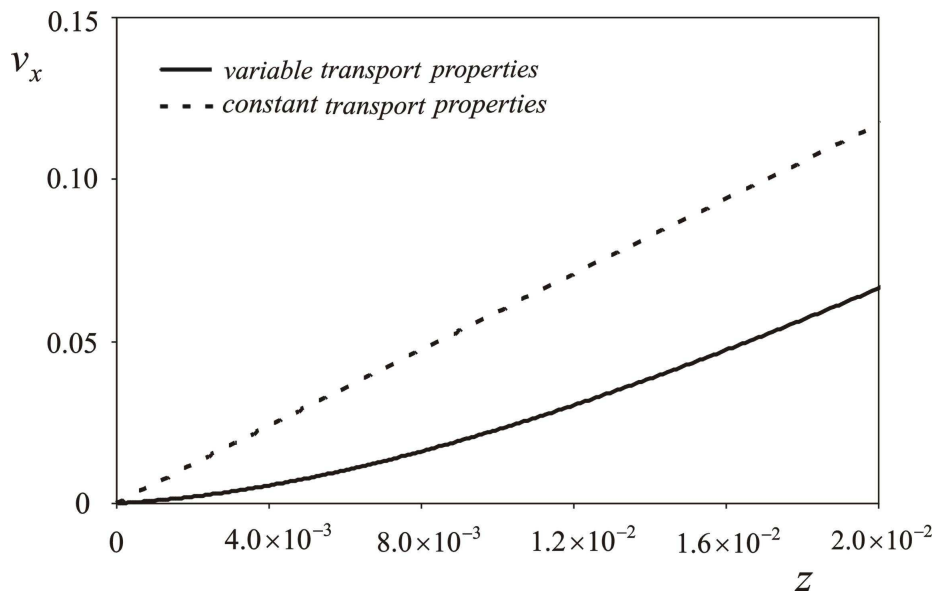


Figure 3.8 – Normalized tangential velocity along the normal direction at the end of the last semi-permeable sub-section ($x = 580$) – lines I-J of Figure 7 ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $Pe_{BSA}^0 = 2.37 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$; $v_f = 1 \times 10^{-6}$; $\Delta P = 2.43 \times 10^5 \text{ Pa}$; $n = 4$).

A higher viscosity at the semi-permeable membrane surface [16, 17] induces a lower value of the tangential velocity (Figure 3.8) and, as a result, a stronger accumulation of solutes (BSA and Dextran-T10) at the semi-permeable membrane surface.

3.7.3.2. Ratio between concentrations of BSA and Dextran-T10 along normal and tangential directions

For a better understanding of what happens in the fractionation process, the concentrations of BSA and Dextran-T10 along the line I-J (Figure 3.7) are represented in Figure 3.9, for variable transport properties (case 1) and for constant transport properties (case 2).

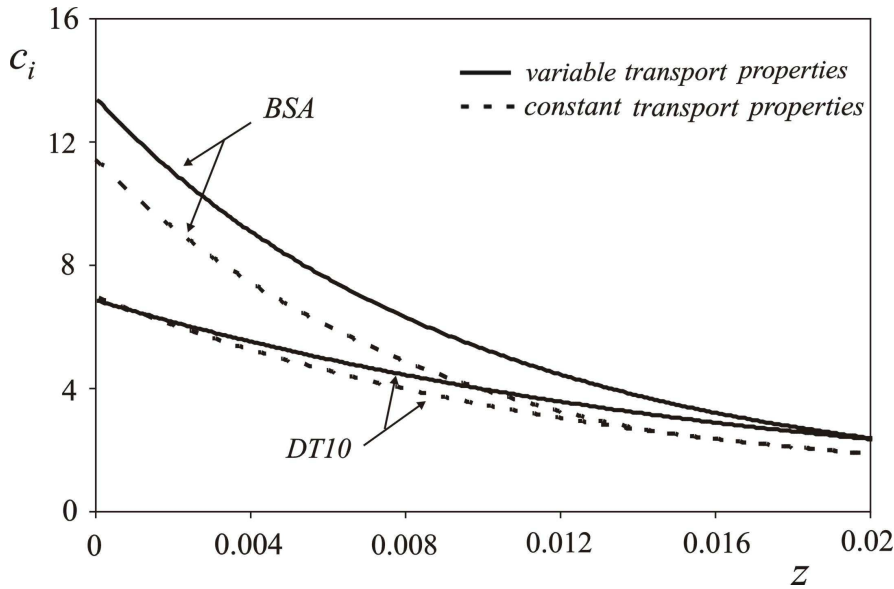


Figure 3.9 – Normalized concentration profiles along the normal direction, z , at the last semi-permeable sub-section ($x = 580$) – lines I-J of Figure 7 ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $Pe_{BSA}^0 = 2.37 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$; $v_f = 1 \times 10^{-6}$; $\Delta P = 2.43 \times 10^5 \text{ Pa}$; $n = 4$).

The cross-section represented by line I-J (at the end of the last semi-permeable sub-section) is crossed by all the fluid (see streamlines in Figure 3.7) that is going to materialize the concentrate stream. Along this cross-section, the concentration of the component with the lower diffusivity, BSA, is higher than the concentration of Dextran-T10. This behaviour is maintained along the trajectories of the fluid until it crosses the fully-permeable membrane.

The ratio between the concentrations of BSA and Dextran-T10, along the normal direction to the semi-permeable membrane is significantly higher for variable properties (relative difference around 15 to 20%), since the accumulation of BSA is higher, due to the reasons explained above.

Figure 3.10 shows the ratio between the concentrations of BSA and Dextran-T10 along the membrane surface at the end of the last semi-permeable sub-section and at the beginning of the last fully permeable sub-section ($n = 4$) for variable (case 1) and constant properties (case 2). Along the semi-permeable sub-section, the ratio is significantly higher for variable transport properties (relative difference around 25%). The BSA accumulation is preferentially removed through the fully-permeable sub-section.

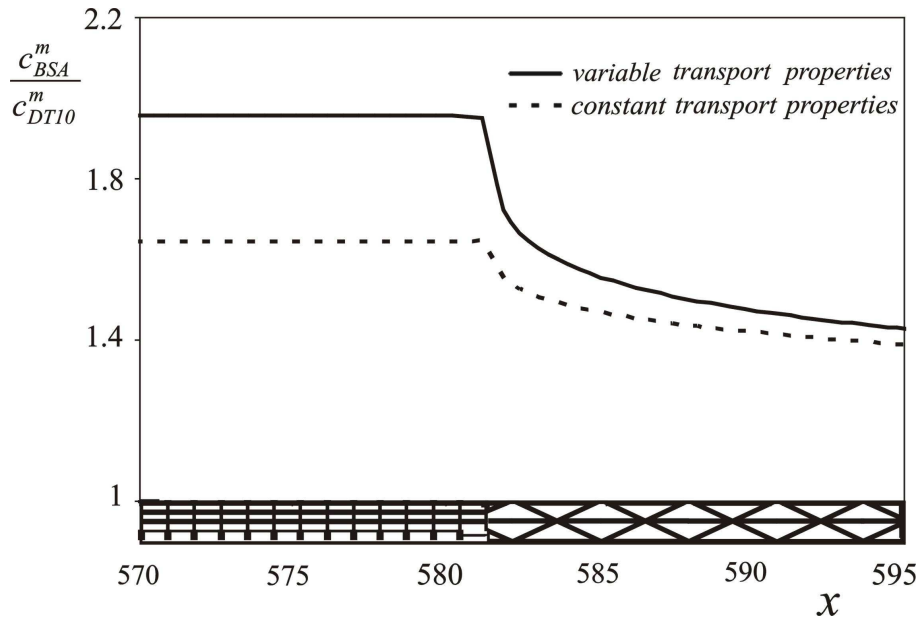


Figure 3.10 – Ratio between normalized concentration of BSA and DT10 at the membrane surface, along the tangential direction, x , at the end of the last semi-permeable sub-section and beginning of the last fully-permeable sub-section ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $Pe_{BSA}^0 = 2.37 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$; $v_f = 1 \times 10^{-6}$; $\Delta P = 2.43 \times 10^5 \text{ Pa}$; $n = 4$).

3.7.3.3. Effect of the viscosity of the concentrate stream in the separation of BSA/DT10

As referred in section 3.7, the results presented in the above sections were obtained using the viscosity of the feed stream. However, the viscosity of the concentrate stream varies

along the fully-permeable membranes due to the longitudinal concentration profiles of the solutes. Figures 3.11a and 3.11b compare results obtained for constant viscosity, evaluated at the concentrations of the feed, with those for variable viscosity, evaluated at the local concentrations.

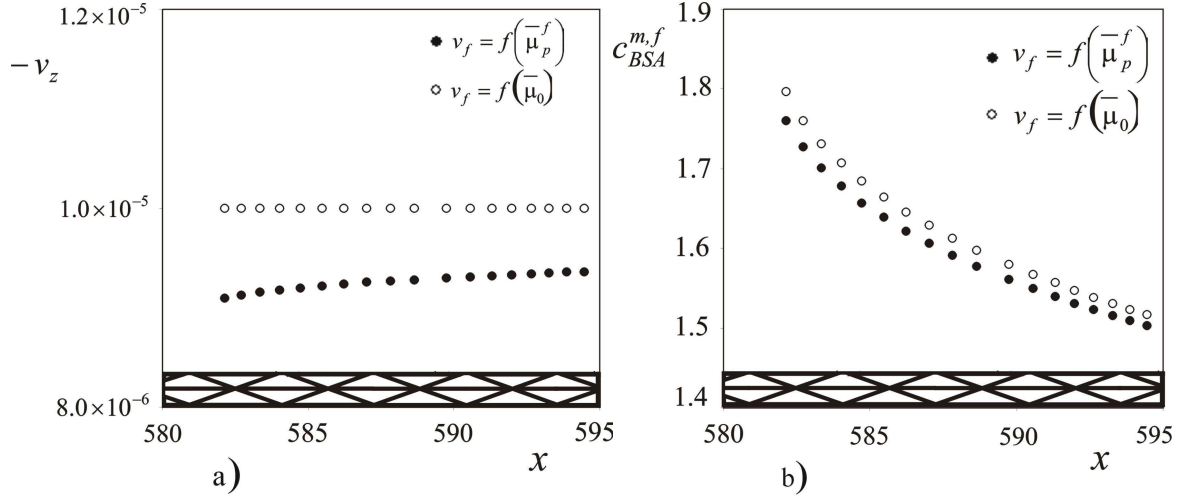


Figure 3.11 – a) Normalized velocity at the membrane surface along the tangential direction, x , b) BSA normalized concentration at the membrane surface along the tangential direction, x , at the beginning of the last fully-permeable sub-section, taking into consideration variable and constant viscosity of the concentrate stream ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $\text{Re}_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $\text{Pe}_{BSA}^0 = 2.37 \times 10^7$; $\text{Pe}_{DT10}^0 = 1.55 \times 10^7$; $\Delta P = 6.08 \times 10^4 \text{ Pa}$; $n = 4$).

Figure 3.11a illustrates the effect of the viscosity on the velocity of the concentrate stream. The velocity is lower for the viscosity evaluated with local concentrations, because these concentrations are higher than those in the inlet stream. For variable viscosity, the permeate velocity increases slightly along the fully permeable section because the solute concentrations decrease along the membranes. Figure 3.11b compares the concentration of BSA along the surface of a fully-permeable membrane for both cases in study. BSA concentration is lower for concentration dependent viscosity because permeate velocity is also lower.

3.7.3.4. Effect of the osmotic pressure in the separation of BSA/DT10

Figures 3.12a and 3.12b illustrate the effect of the osmotic pressure on the separation. Osmotic pressure contributes to reduce the effective transmembrane pressure through the semi-permeable sub-sections, and consequently, to reduce the permeate velocity. Figure

3.12a shows that the permeate velocity, when osmotic pressure is neglected (case 3), is higher than the permeate velocity when the effect of the osmotic pressure is taken into account (case 1).

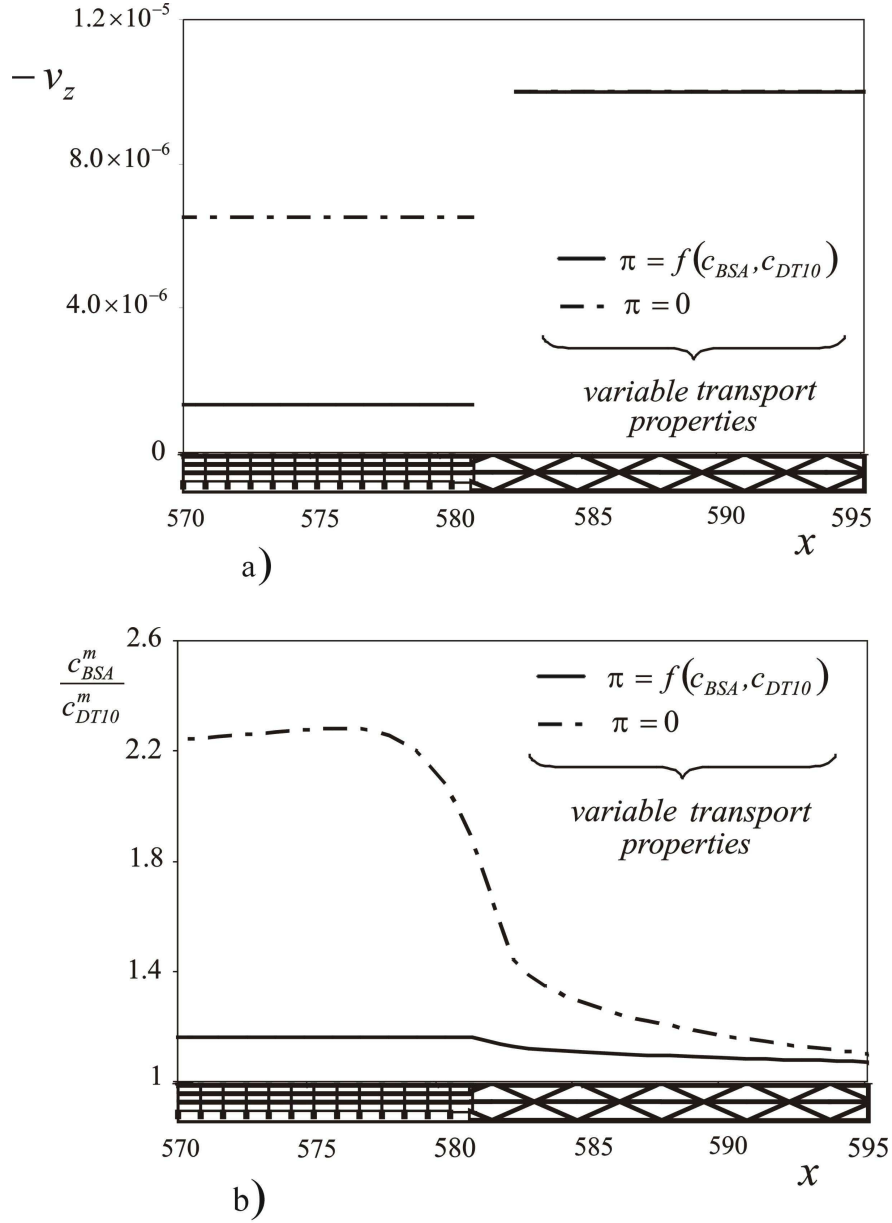


Figure 3.12 – a) Normalized velocity at the membrane surface along the tangential direction, x , b) Ratio between the normalized surface concentrations of BSA and Dextran-T10 along the tangential direction, x , at the end of the last semi-permeable sub-section and beginning of the last fully-permeable sub-section ($C_{BSA}^{in} = 24.4 \text{ kg/m}^3$; $C_{DT10}^{in} = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632 \text{ m/s}$; $Pe_{BSA}^0 = 2.37 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$; $v_f = 1 \times 10^{-5}$; $\Delta P = 6.08 \times 10^4 \text{ Pa}$; $n = 4$).

Lower permeate velocities induces lower concentrations near the semi-permeable membrane. In the case of BSA/Dextran-T10, this decrease is higher in the component that accumulates more over the semi-permeable membrane (BSA). The concentration ratio is therefore smaller (case 1) when the effect of the osmotic pressure is considered (Figure 3.12b). Consequently, the concentration ratio in the stream recovered in the fully-permeable membrane is also smaller (Figure 3.12b). In conclusion, the osmotic pressure has a negative effect on the separation by differential diffusivity in hybrid membrane cells.

3.8. Conclusions

The main objective was to study the effect of the variation of the transport properties with the concentration of solutes in a Hybrid Membrane Cell, where the separation of two macromolecules (BSA/Dextran-T10 or BSA/Lysosyme) takes place by a differential diffusivity mechanism.

The ratios between concentrations of BSA/DT10 system and BSA/LYS system at the semi-permeable membrane surface and the purity of BSA were analyzed for low and high concentration polarization of the semi-permeable membrane surface and for different values of the permeate velocity through fully-permeable membranes. For low levels of concentration polarization (low applied pressure difference), the effect of variable properties is not important since the accumulation of both components at the semi-permeable membrane surface is low and the separation is practically inexistent.

For high levels of concentration polarization, the variation of the transport properties (viscosity increase and diffusivity decrease) determines the separation. For BSA/DT10 system, this variation promotes BSA (the component with less diffusivity) accumulation at the surface of the semi-permeable membrane which, in turn, induces an increase in the purity of BSA in the outgoing stream current, i.e., in the flow through the contiguous fully permeable membrane. This increase can reach, according to the operating parameters, 20% of the separation obtained by differential diffusion. This increase is higher for low values of the permeate velocity through the fully permeable membranes.

For the separation of BSA/LYS and higher levels of concentration polarization, the purity of BSA decreases if the variation of the transport properties is taken on account. This decrease comes from the higher (in percentage) accumulation of LYS (relatively to BSA) at the semi-permeable membranes surface due to the variation of the transport properties. The diffusivity of LYS is much lower than that of DT10, main reason of this opposite behaviour. The BSA purity decrease can reach 6% of the separation obtained by differential diffusion.

The concentration and flow fields and the ratio between concentrations along normal and tangential directions were studied in detail for BSA/Dextran-T10 separation. The effect of the viscosity in the concentrate stream and the effect of the osmotic pressure were also studied. The results show that the osmotic pressure has a negative effect on the separation by differential diffusivity in hybrid membrane cells because the concentration of the component with lower diffusivity (BSA) is more sensitive to variations of the permeate velocity.

In a future work, we intend to study this fractionation process including the transmission of the solutes through the semi-permeable membranes and the electric interactions between the molecules of the solutes and a charged semi-permeable membrane.

3.9. Nomenclature

C_i	Concentration of component i
C_i^{in}	Concentration of component i at the feed stream
c_i	Normalized concentration of component i
c_i^m	Normalized concentration of component i at membrane surface
$c_i^{m,f}$	Normalized concentration of component i at fully-permeable membrane sub-sections
$c_i^{m,s}$	Normalized concentration of component i at semi-permeable membrane sub-sections
$\bar{c}_i^{m,s}$	Mean normalized concentration of component i at semi-permeable membrane surface
D_i	Diffusivity of component i
$E\mu_0$	Euler parameter

H	Distance between parallel plates
k_1^i	First virial coefficient of the osmotic pressure of component i
k_2^i	Second virial coefficient of the osmotic pressure of component i
k_3^i	Third virial coefficient of the osmotic pressure of component i
L_{out}	Length of the outlet section
l_{out}	Normalized length of the outlet section
L_{in}	Length of the inlet section
l_{in}	Normalized length of the inlet section
L_m	Total length of the membrane sections
l_m	Total normalized length of the membrane sections
L	Length of the cell
L	Normalized length of the cell
L_s	Length of a semi-permeable membrane sub-section
l_s	Normalized length of a semi-permeable membrane sub-section
L_f	Length of a fully permeable membrane sub-section
l_f	Normalized length of a fully-permeable membrane sub-section
n	Number of sections of the HMC
ni_m	Number of grid nodes at membrane surface
p	Non-dimensional pressure
$Pu_{BSA}(\%)$	Purity of BSA relatively to the mixture of BSA and component j
$Pu_{BSA}^{in}(\%)$	Purity of BSA relatively to the mixture of BSA and component j for low applied pressure difference
R_m	Membrane resistance
R_m^s	Membrane resistance of the semi-permeable membrane sub-sections
R_m^f	Membrane resistance of the fully-permeable membrane sub-sections
R_t	Total residue
R_ω	Residue of the vorticity equation
$R_{c_i}^m$	Residue of the mass transport equation of component i
S	Source term of the vorticity transport equation
t	Time
V_0	Feed velocity

V_m	Velocity at semi-permeable membrane surface
v_x	Normalized longitudinal component of the velocity
v_z	Normalized normal component of the velocity
v_f	Normalized permeate velocity at fully permeable membrane sub-sections
v_s	Normalized permeate velocity at semi-permeable membrane sub-sections
x_i	Mass fraction of component i
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Z	Transversal coordinate
z	Normalized transversal coordinate
W	Width of the cell

Non-dimensional numbers

Pe_i	Peclet number of component i
Pe_i^0	Inlet Peclet number of component i
Re	Reynolds number
Re_0	Inlet Reynolds number
Π_v	equation 3.24
Π_{π_0}	$\frac{\Pi_0}{\Delta P}$
$(\Pi_{\pi_0}^i)_1$	equation 3.25
$(\Pi_{\pi_0}^j)_1$	equation 3.26
$(\Pi_{\pi_0}^i)_2$	equation 3.25
$(\Pi_{\pi_0}^j)_2$	equation 3.26
$(\Pi_{\pi_0}^i)_3$	equation 3.25
$(\Pi_{\pi_0}^j)_3$	equation 3.26

Greek Symbols

ΔP	Static pressure difference across a semi-permeable membrane
ΔP_{eff}	Effective static pressure difference across a semi-permeable membrane

ΔP^f	Static pressure difference across a fully-permeable membrane
$\epsilon_{-m,s}$ c_i	Discretization error
ϵ_{crit}	Critic error in two consecutive iterations
π_i	Osmotic pressure of component i
π_i^m	Osmotic pressure of component i at semi-permeable membrane surface
$\Delta\pi_{i/j}$	Osmotic pressure difference of a solution of component i and j at semi-permeable membrane
ψ	Stream function
ω	Vorticity
ρ	Density
μ_i	Viscosity of a solution of the component i
$\bar{\mu}$	Viscosity of the solution of BSA and component j
$\bar{\mu}_0$	Viscosity of the solution of BSA and component j at the inlet
$\bar{\mu}_p^s$	Viscosity of the permeate flux at semi-permeable membrane sub-sections
$\bar{\mu}_p^f$	Viscosity of the permeate flux at fully-permeable membrane sub-sections
ϕ_i	$\ln(c_i)$

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Chapter 4

The apparent selectivity in the fractionation of BSA and Dextran-T10 by ultrafiltration – a CFD study

The fractionation of BSA and Dextran-T10 by ultrafiltration in a parallel plate cell was studied by numerical methods. The study takes on account the pressure drop and the variation of the permeate velocity along the cell, the concentration polarization over the membrane and the variation of the transport properties and of the osmotic pressure with the concentration of the solutes. A convective-diffusive model, to simulate the solute transmission, was adopted. The real and the apparent selectivity, local and mean, were determined, in order to study the effect of the transmembrane pressure, Reynolds number, inlet solute concentrations, specific area of the membrane pores and resistance of the membrane. From the numerical data, it is shown that concentration polarisation increases the apparent transmission of the solutes and reduces the apparent selectivity of the separation process. For high feed concentrations, the concentration dependent transport properties contribute to reduce selectivity.

The contents of this chapter were adapted from: S.I.S. Pinto, J.M. Miranda, J.B.L.M. Campos, The apparent selectivity in the fractionation of BSA and Dextran-T10 by ultrafiltration – a CFD study, submitted for publication in the *AIChE Journal* (2011).

4.1. Introduction

In the latest years, the fractionation of macromolecules, mainly proteins, by ultrafiltration has gained relevance; the advantages are a high throughput and an easy scale-up. Most of the times, this separation is difficult to perform, since the solutes are very similar in size [1, 2]. Nevertheless, the fractionation of macromolecules by ultrafiltration has attracted a considerable amount of attention in such diversified fields as biotechnology, biomedicine and food industry.

The binary solute fractionation by ultrafiltration is based on a differential of pressure imposed across the membrane. Additionally, the solutes have a selective passage across the membrane, i.e., a preferential retention of one of the solutes and a simultaneous preferential transmission of the other [3].

Several studies have shown that concentration polarisation of the membrane increases the apparent transmission of proteins across the membrane and reduces the apparent selectivity of the separation process. Müller et al. [4] found that high crossflow velocities, which promote depolarization, reduced the transmission of lysozyme and myoglobin, but at the same time, increased the selectivity of the permeate flow. Agarwal [5] studied the transmission of BSA and ovalbumin in an ultrafiltration vortex flow module. According to the author, the apparent transmission increased with the decrease of the rotation speed, which means that transmission increased with concentration polarization. Li et al [6] studied the effect of gas sparging in the fractionation of HSA and IgG. They observed reversed selectivity, i.e., HSA is the smaller molecule but it was the component with the highest rejection. Reversed selectivity was explained by the electrical repulsion between HSA and the membrane. Gas sparging caused the reduction of the permittivity of both components. The permittivity of HSA was the most reduced, which led to an increase in the selectivity. Gosh et al. [7] studied the effect of gas sparging in the fractionation of BSA and Lysozyme by ultrafiltration. BSA was the less transmitted component. The authors also found that gas sparging reduced the transmission of both BSA and Lysozyme. The effect was higher for BSA, which led to an increase of the selectivity. Kaur and Agarwal [8] studied the effect of a flow with Dean vortices in the transmission of proteins. The authors found that the transmission of lysozyme increases with the decrease of the crossflow velocity. Balakrishnan

and Agarwal [9] studied the protein fractionation in a vortex flow filter where they measured the transmission of lysozyme, ovalbumin and myoglobin. The transmissions of ovalbumin and myoglobin decreased with the rotation speed. However, the transmission of lysozyme increased with the increase of the rotation speed reaching values above 100%. According to the authors, these anomalous effects can be explained by electric interactions. In a subsequent work [10], Balakrishnan and Agarwal studied the effect of rotation in the fractionation of mixtures of lysozyme and ovalbumine. The transmission of lysozyme increased and the transmission of ovalbumine decreased with an increase of the rotation speed, leading to an increase of the selectivity.

The mechanism by which concentration polarization reduces selectivity is complex, since it may involve diffusion and convection across the membrane and solute-solute and solute-membrane interactions. When electric interactions can be neglected, the phenomenon is usually studied with a model that combines the film equation with a model for convection-diffusion of solutes across the membrane. The film model is often used to interpret protein fractionation results. For example, Gosh et al. [7] found that their transmission results were consistent with a simple model based on the film equation with a constant sieving coefficient. Kaur and Agarwal [8] found that their results were compatible with the film model combined with a convection-diffusion model for mass transport across the membrane. The film model was also used by Gosh and Cui [3] to simulate protein fractionation by ultrafiltration. The authors combined the film model with a convection-diffusion model of solute transmission across the membrane to determine the influence of the permeate velocity in the selectivity.

There are, however, a number of significant limitations and shortcomings to the stagnant film analysis. A simple film model is unable to deal with solute-solute interactions [11], concentration dependent properties and solute-membrane interactions. A number of attempts have been made to address these limitations by modifying the film model. Most of them have focused on the effects of a concentration dependent viscosity, diffusivity and osmotic pressure [12-14].

Shen and Probstein [15] developed a numerical solution to the mass and momentum transfer equations for cross-flow filtration using more general expressions for the concentration dependence of the viscosity of the solution and the diffusivity of the solutes.

The results were relatively insensitive to the variation in viscosity, in sharp contrast to the conclusions of Aimar and Field [13] and Meien and Nobrega [14]. However, the permeate flux was significantly affected by the concentration dependence of the solute diffusivity. Shen and Probstein [15] assumed that the filtration velocity was constant, which is equivalent to neglect osmotic pressure effects. This assumption makes difficult the application of their results to realistic separation membrane systems.

Saksena and Zydney [11] developed a generalized framework for multicomponent separation. They solved the governing conservation equations incorporating the multicomponent diffusive flux. The hydrodynamic model was that of a stirred cell, where the velocity profiles were approximated by solving analytically the continuity and momentum equations for the flow of a rotating fluid (with constant viscosity) near a stationary wall in an unbounded system.

With the advancements in computing, the CFD approach has been reported in several studies of concentration polarization and solute transport in various membrane separation systems [16-19]. These studies have shown that direct simulation can provide indispensable details of the flow and solute transport process, and even of the interactions between the flow and solute transport, in such membrane systems.

As far as we know, there is no complete CFD study concerning the solution of the conservative mass and flow equations with variable physical properties and thermodynamic effects for the fractionation of two solutes. The present numerical study was applied to quantify the influence of the polarisation phenomenon in the apparent selectivity of the fractionation of Bovine Serum Albumin (BSA) and Dextran-T10 in a parallel plate membrane cell. The apparent selectivity was obtained by solving the conservative equations with a convective-diffusive model for the transport of solutes across the membrane [20, 21].

4.2. Cell description

The cell under study is schematically represented in Figure 4.1. It is a parallel plate cell with a permeable membrane on both sides. The membrane is permeable to the solvent and

partially permeable to both solutes (BSA and Dextran-T10), according to the local rejection coefficients, which depend on the local permeate velocity and solute concentration.

The distance between the plates is H , the width and length of the cell are W and L , respectively. The feed stream is separated into two streams: a retentate stream and a permeate stream. The retentate stream is richer in solute with the lower transmission – BSA – and the permeate stream is richer in solute with the higher transmission – Dextran-T10. The inlet (L_{in}) and outlet (L_{out}) sections are both impermeable to the solutes and to the solvent.

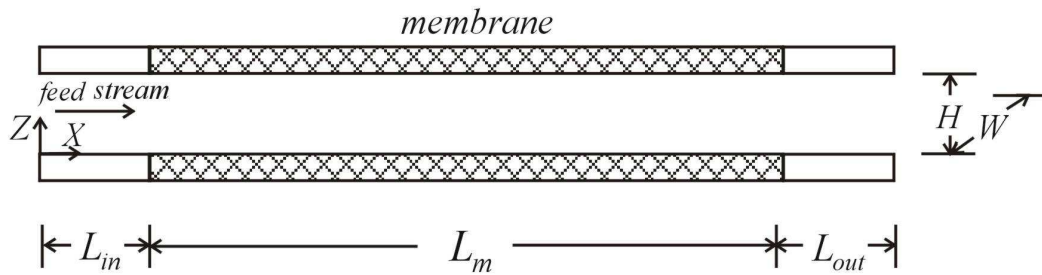


Figure 4.1 – Schematic representation of the cell.

The characteristics of the parallel plate cell are listed in Table 4.1.

Table 4.1 - Characteristics of the cell.

Membrane	Polysulfone membrane, 50 kDa MWCO
$R_m \text{ (m}^{-1}\text{)}$	5.714×10^{12}
$H \text{ (m)}$	0.001
$L_m \text{ (m)}$	0.50

4.3. Theory

4.3.1. Features and assumptions of the model

The solution of the conservative equations by CFD enables the determination of accurate hydrodynamic and concentration fields along the membrane. A steady state solution is achieved based on the solution of the transient flow and mass transport equations. The results presented are the steady state values. The following items are taken into account:

1. The change of the permeate velocity and of the concentration of the solutes along the membrane surface;
2. The concentration dependence of the transport properties, viscosity of the solution and diffusivity of the solutes, and also the non-linear concentration dependence of the osmotic pressure;
3. The selective passage of the solutes through the membrane, according to a diffusive-convective model.

Even so, some assumptions must be made:

1. The flow regime is laminar;
2. Electric interactions between solutes and between solutes and membrane are not considered;
3. The transport parameters for a particular solute are assumed to be identical for single and binary mixture ultrafiltration;
4. Uniform fluid density, since its variation is not significant in the concentration range of interest;
5. The fouling at membrane surface, which could change the sieving properties, is not taken in consideration.

4.3.2. Transmission and selectivity

The real transmission of a solute i is expressed in the literature by the true sieving coefficient (S_i), which is the ratio between the concentration of the solute in the permeate (C_i^p) to that at the membrane surface (C_i^m):

$$S_i = \frac{C_i^p}{C_i^m} \quad (4.1)$$

The rejection of a solute i is then given by:

$$R_i = \frac{C_i^m - C_i^p}{C_i^m} = 1 - S_i \quad (4.2)$$

The real selectivity (σ) quantifies the efficiency of the solute fractionation and it is defined by:

$$\sigma = \frac{S_i}{S_j} = \frac{1-R_i}{1-R_j} \quad (4.3)$$

However, the so-called apparent sieving coefficient (S_{ap_i}), which is defined by the ratio between the concentration of a solute i in the permeate (C_i^p) and that in the bulk (C_i^0), is much more suitable to handle experimental data:

$$S_{ap_i} = \frac{C_i^p}{C_i^0} \quad (4.4)$$

The apparent selectivity (σ_{ap}) is then defined by:

$$\sigma_{ap} = \frac{S_{ap_i}}{S_{ap_j}} = \frac{C_i^p / C_i^0}{C_j^p / C_j^0} \quad (4.5)$$

where i represents the preferentially transmitted solute (Dextran-T10) and j the preferentially rejected solute (BSA).

4.3.3. Diffusive and convective transport across the membrane

According to the model of Opong and Zydney [21], the solutes are transmitted across the membrane by diffusive and convective mechanisms. The total flux of solute i through the membrane is then given by:

$$N_i = K_i^c V_m C_i - K_i^d D_{i,\infty} \frac{dC_i}{dZ} \quad (4.6)$$

where C_i is the concentration of component i , V_m the permeate velocity, $D_{i,\infty}$ the free diffusivity of component i and K_i^c and K_i^d are, respectively, the convective and diffusive hindrance factors of component i .

The model developed by Opong and Zydney [21] enables the determination of the true sieving coefficient of each component along the membrane, which is function of the permeate velocity, V_m :

$$S_i = \frac{S_{i,\infty} \exp\left[(S_{i,\infty} V_m \delta_m) / D_{i,eff}\right]}{S_{i,\infty} + \exp\left[(S_{i,\infty} V_m \delta_m) / D_{i,eff}\right] - 1} \quad (4.7)$$

where $S_{i,\infty}$ is the asymptotic intrinsic sieving coefficient of component i , δ_m the membrane thickness and $D_{i,eff}$ the effective diffusivity of component i along the membrane pore.

According to the definition (equation 4.2), the rejection coefficient of component i is then given by:

$$R_i = 1 - \frac{S_{i,\infty} \exp\left[(S_{i,\infty} V_m \delta_m) / D_{i,eff}\right]}{S_{i,\infty} + \exp\left[(S_{i,\infty} V_m \delta_m) / D_{i,eff}\right] - 1} \quad (4.8)$$

According to Opong and Zydney [21], the asymptotic intrinsic sieving coefficient of the component i is proportional to the hindrance factor K_i^c :

$$S_{i,\infty} = \phi_i^p K_i^c \quad (4.9)$$

with the constant of proportionality, ϕ_i^p , representing the equilibrium partition coefficient.

This coefficient is, once again according to Opong and Zydney [21], given by:

$$\phi_i^p = (1 - \lambda_i) , \quad 0 < \lambda_i < 1 \quad (4.10)$$

where the parameter λ_i depends on the equivalent molecular radius of the component i , r_i^* , and on the specific area of the pores of the membrane, s :

$$\lambda_i = \frac{r_i^*}{2s} \quad (4.11)$$

The equivalent molecular radius of the molecules of BSA and Dextran-T10 and the values of the parameter λ_i for the OMEGA Polysulfone Membrane 50 kDa MWCO are listed in Table 4.2. The equivalent molecular radius of BSA was determined based on data from Tencer et al. [22] and the equivalent molecular radius of Dextran-T10 was taken from Granath [23]. The specific area of the pores of the membrane was determined based on experimental data of Opong and Zydney [21].

Table 4.2 - Values of λ_i .

Component	r_i^* (nm)	λ_i
BSA	3.04	0.830
DextranT10	2.36	0.645

The convective and diffusive hindrance factors, K_i^c and K_i^d , which are dependent on the values of λ_i , were also determined in the present study according to Opong and Zydney [21].

4.3.4. Physical properties

Dextran is a complex polysaccharide made of many glucose molecules used medicinally as an antithrombotic and to reduce blood viscosity. Dextran is also used in the osmotic stress technique for applying osmotic pressure to biological molecules. Dextrans are available in multiple molecular weights ranging from 10 000 Da to 150 000 Da.

Bovine Serum Albumin (BSA) is a protein that has numerous biochemical applications and it is also used as a nutrient in microbial cultures. The molecular weight of this protein is around 69 000 Da.

A solution with pH = 4.7 and ionic strength of 0.15 M (at the BSA isoelectric point) was considered in the present study. The diffusivity and the osmotic pressure of BSA solutions are affected by the pH and by the ionic strength, and so care was taken choosing, in the literature, correlations of these physical properties for pre-defined values of pH and ionic strength. The diffusivity of a protein in solution depends on the interactions between the molecules. These interactions change with the concentration of the protein and also with the associated charge. The charge is function of the pH of the solution and has a minimum value at the isoelectric point. At the isoelectric point, the interactions are minimum and so it is the diffusivity of the protein. The low diffusivity in the vicinity of the membrane, at the isoelectric point, increases the accumulation of the protein at the membrane surface.

The viscosity and diffusivity data of individual solutions of BSA and Dextran-T10 are represented in Table 4.3.

Table 4.3 – Viscosity, diffusivity and osmotic pressure of BSA and Dextran-T10.

<i>Equations</i>		
<i>Property</i>	BSA	Dextran-T10
Viscosity (Pa.s)	$\mu_{BSA} = 9.086 \times 10^{-4} \exp(2.44 \times 10^{-5} C^2) \quad (4.12)$ Gill et al. [24]	$\mu_{DT10} = 10^{-3} + 1.85 \times 10^{-5} C - 5.0 \times 10^{-8} C^2 + 6.67 \times 10^{-10} C^3 \quad (4.13)$ Field and Aimar [25]
Diffusivity (m ² /s)	$D_{BSA} = (7 - 0.0041C) \times 10^{-11} \quad (4.14)$ Leung and Probstein [26]	$D_{DT10} = 10.5 \times 10^{-11} \quad (4.15)$ S. De and P. K. Bhattacharya [27]

The diffusivity of Dextran-T10 is taken constant [27]. Laurent et al. [28] studied the diffusivity of Dextran-T19 and Dextran-T150. The data showed that the diffusivity of Dextran-T19 is almost constant ($7.2\text{--}7.4 \times 10^{-10}$ m²/s) in a large range of solute concentration (from diluted solutions to concentrations around 100 kg/m³). The behaviour is different for the solution of higher molecular weight (Dextran-T150): a variation of 270% for the same range of solute concentration was found. The study of Laurent et al. [28] suggests that for Dextran-T10, it is reasonable to assume a constant diffusion coefficient (10.5×10^{-11} m²/s) [27], when there are no further detailed reports on the concentration dependency in the literature.

The viscosity of the mixture ($\bar{\mu}$) was obtained by:

$$\bar{\mu} = \mu_{BSA} x_{BSA} + \mu_{DT10} x_{DT10} \quad (4.16)$$

where x_{BSA} and x_{DT10} are the mass fractions of BSA and Dextran-T10, respectively.

The Reynolds number is based on the channel height; option adopted for an easier comparison with data from literature:

$$Re = \frac{\rho V_0 H}{\mu} \quad (4.17)$$

where, the density of the mixture (ρ) is taken constant and equal to the inlet density and V_0 represents the inlet velocity. Note that the Reynolds number based on the hydraulic diameter, $d_h = 2H$, is two times higher than that defined by equation 4.17.

The Peclet numbers, Pe_{BSA} and Pe_{DT10} , are by definition:

$$Pe_{BSA} = \frac{V_0 H}{D_{BSA}}, Pe_{DT10} = \frac{V_0 H}{D_{DT10}} \quad (4.18)$$

The osmotic pressure of each component, BSA and Dextran-T10, is non-linearly dependent on the respective concentration:

$$\pi_i = k_1^i C_i + k_2^i C_i^2 + k_3^i C_i^3 \quad (4.19)$$

The values k_1^i , k_2^i and k_3^i were obtained from Jonsson [29] (Dextran-T10) and from Leung and Probstein [26] (BSA). These values are listed in Table 4.4.

Table 4.4 - Values of k_1^i , k_2^i and k_3^i for each solute.

	BSA	Dextran-T10
k_1^i	2.3×10^2 [a]	1.116×10^3 [b]
k_2^i	-1.34 [a]	-4.91 [b]
k_3^i	3.09×10^{-3} [a]	2.57×10^{-2} [b]

[a] Leung and Probstein [26]

[b] Jonsson [29]

4.3.5. Flow and mass transport equations

The Navier-Stokes equations for concentration dependent viscosity and Cartesian coordinates (x along the flow direction and z normal to the flow direction) normalized by the height of the cell are:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0 \quad (4.20)$$

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_x}{\partial z} = -Eu_0 \frac{\partial p}{\partial x} + \left[\frac{\partial \left(2 \frac{1}{Re} \frac{\partial v_x}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{1}{Re} \frac{\partial v_z}{\partial x} + \frac{1}{Re} \frac{\partial v_x}{\partial z} \right)}{\partial z} \right] \quad (4.21)$$

$$\frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_z \frac{\partial v_z}{\partial z} = -Eu_0 \frac{\partial p}{\partial z} + \left[\frac{\partial \left(2 \frac{1}{Re} \frac{\partial v_z}{\partial z} \right)}{\partial z} + \frac{\partial \left(\frac{1}{Re} \frac{\partial v_z}{\partial x} + \frac{1}{Re} \frac{\partial v_x}{\partial z} \right)}{\partial x} \right] \quad (4.22)$$

The above equations can be written for secondary variables (vorticity, ω , and stream function, ψ):

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} \quad (4.23)$$

$$\frac{\partial \omega}{\partial t} + \left(v_x - 2 \frac{\partial}{\partial x} \frac{1}{Re} \right) \frac{\partial \omega}{\partial x} + \left(v_z - 2 \frac{\partial}{\partial z} \frac{1}{Re} \right) \frac{\partial \omega}{\partial z} = \omega \left(\frac{\partial^2}{\partial x^2} \frac{1}{Re} + \frac{\partial^2}{\partial z^2} \frac{1}{Re} \right) + \frac{1}{Re} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial z^2} \right) + S \quad (4.24)$$

where S is:

$$S = -2 \left(\frac{\partial^2}{\partial x^2} \frac{1}{Re} \frac{\partial^2 \psi}{\partial z^2} - 2 \frac{\partial^2}{\partial x \partial z} \frac{1}{Re} \frac{\partial^2 \psi}{\partial x \partial z} + \frac{\partial^2}{\partial z^2} \frac{1}{Re} \frac{\partial^2 \psi}{\partial x^2} \right) \quad (4.25)$$

Equation (4.23) is a Poisson-type equation and equation (4.24) is the vorticity transport equation for variable viscosity. The dimensionless stream function ψ is defined by:

$$v_x = \frac{\partial \psi}{\partial z} \quad (4.26)$$

$$v_z = -\frac{\partial \psi}{\partial x} \quad (4.27)$$

The velocity field was determined by solving the Poisson-type equation and the vorticity transport equation. These equations were discretized by a finite difference method (for more details see Afonso et al. [30] and Miranda and Campos [31]). The pressure gradient along x was determined by an equation obtained from equation (4.21).

$$\frac{\partial p}{\partial x} = \frac{1}{Eu_0} \left[\frac{\partial \left(2 \frac{1}{Re} \frac{\partial v_x}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{1}{Re} \frac{\partial v_z}{\partial x} + \frac{1}{Re} \frac{\partial v_x}{\partial z} \right)}{\partial z} - v_x \frac{\partial v_x}{\partial x} - v_z \frac{\partial v_x}{\partial z} \right] \quad (4.28)$$

The pressure drop was determined by integrating the pressure gradient along the membrane surface.

The mass transport equation was discretized after a change of variable, $\phi_i = \ln c_i$, in order to linearize the concentration profiles over the membrane [32].

$$\frac{\partial \phi_i}{\partial t} + \left(v_x - \frac{\partial}{\partial x} \frac{1}{Pe_i} - \frac{1}{Pe_i} \frac{\partial \phi_i}{\partial x} \right) \frac{\partial \phi_i}{\partial x} + \left(v_z - \frac{\partial}{\partial z} \frac{1}{Pe_i} - \frac{1}{Pe_i} \frac{\partial \phi_i}{\partial z} \right) \frac{\partial \phi_i}{\partial z} = \frac{1}{Pe_i} \left(\frac{\partial^2 \phi_i}{\partial x^2} + \frac{\partial^2 \phi_i}{\partial z^2} \right) \quad (4.29)$$

This linearization reduces the size of the grid necessary to obtain an accurate solution (for more details see Miranda and Campos [32]).

4.3.6. Domain and numerical grid

The numerical domain represents half of the physical cell (the cell is symmetric) and it is shown in Figure 4.2. The domain comprises an inlet section, an outlet section and the membrane.

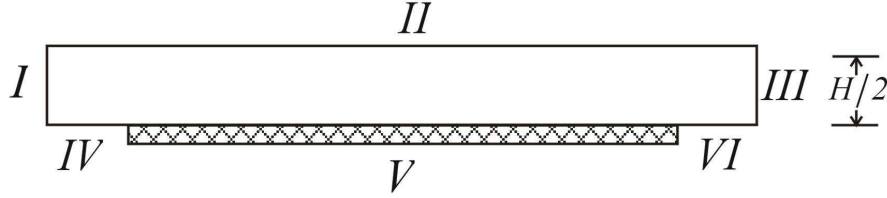


Figure 4.2 – Schematic representation of the numerical domain.

The domain was converted into a grid of discrete nodes. The grid is non-uniform along directions x and z in order to obtain denser regions near the membrane surface and at the beginning and end of the membrane section. To study the accuracy of the discretisation method, grid tests were performed taking the following indicator as discretisation error:

$$\mathcal{E}_{c_i}^{-m} = \left| \frac{\bar{c}_i^{-m,ref} - \bar{c}_i^{-m}}{\bar{c}_i^{-m,ref}} \right| \quad (4.30)$$

with the mean normalized surface concentration of component i of the most refined grid ($\bar{c}_i^{-m,ref}$) as reference.

The results of the grid tests are shown in tables 4.5 and 4.6. The grid with 225×251 nodes has discretisation errors less than 1.2% and was adopted to perform the simulation. This grid is represented in Figure 4.3, where the cell dimensions are given.

Table 4.5 – Grid tests ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$; $C_{DT10}^0 = 24.4 \text{ kg/m}^3$; $\text{Re}_0 = 1387$ ($V_0 = 1.632 \text{ m/s}$); $\text{Pe}_{BSA}^0 = 2.36 \times 10^7$; $\text{Pe}_{DT10}^0 = 1.55 \times 10^7$ and $\Delta P_0 = 2.43 \times 10^5 \text{ Pa}$).

Grid (n × m)	ni_m [a]	$\mathcal{E}_{c_{BSA}}^{-m}$	$\mathcal{E}_{c_{DT10}}^{-m}$
225 × 126	208	3.01%	2.85%
225 × 251	208	1.21%	1.16%
225 × 501	208	ref. grid	ref. grid

[a] ni_m is the number of grid nodes at membrane surface

Table 4.6 – Grid tests ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$; $C_{DT10}^0 = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$ ($V_0 = 1.632 \text{ m/s}$); $Pe_{BSA}^0 = 2.36 \times 10^7$; $Pe_{DT10}^0 = 1.55 \times 10^7$ and $\Delta P_0 = 2.43 \times 10^5 \text{ Pa}$).

Grid (n × m)	ni_m [a]	$\epsilon_{C_{BSA}^m}^-$	$\epsilon_{C_{DT10}^m}^-$
121 × 251	104	0.35%	0.18%
225 × 251	208	0.01%	0.02%
433 × 251	416	<i>ref. grid</i>	<i>ref. grid</i>

[a] ni_m is the number of grid nodes at membrane surface

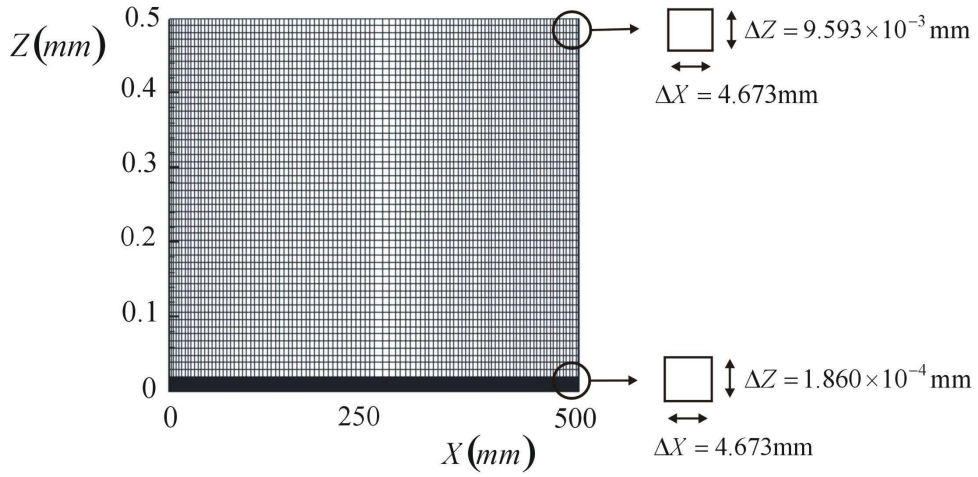


Figure 4.3 – Dimensions of the grid.

4.3.7. Boundary conditions

From here on, all the uppercase variables are dimensional variables and the lowercase normalised variables: the velocities are normalized by the mean feed velocity, V_0 , the concentrations by the feed concentration, C_0 , and the normal and longitudinal coordinates by the height, H , of the cell.

Most of the boundary conditions are listed in previous studies published by Afonso et al. [30] and Miranda and Campos [31, 32]. Succinctly:

- At the cell inlet - boundary I in Figure 4.2- the flow is parallel to the walls, $v_z = 0$; the velocity profile is a well developed laminar one, $v_x = \frac{3}{2} [1 - 4 \times (0.5 - z)^2]$; the normalized concentration of each solute is $c_i = 1$.

- The middle plane - boundary II in Figure 4.2 - is a plane of symmetry and so the momentum and mass fluxes and the pressure variation are null, $\frac{\partial v_x}{\partial z} = 0, \frac{\partial v_z}{\partial z} = 0$ and $\frac{\partial c_i}{\partial z} = 0$.

- At the cell exit - boundary III in Figure 4.2 - it is assumed a fully developed laminar velocity profile, $\frac{\partial v_x}{\partial x} = 0, \frac{\partial v_z}{\partial x} = 0$, and also fully developed solute profiles, $\frac{\partial c_i}{\partial x} = 0$.

At the membrane surface, the fluid has no velocity component along x (no-slip condition). In a pressure driven process the permeate velocity, $v_m = -v_z(x, 0)$, can be expressed by the ratio between the driving force and the resistance to the flow [33]:

$$v_m = \frac{\Delta P_0 - \Delta P_x - (\Delta \pi_{BSA} + \Delta \pi_{DT10})}{\mu_p R_m V_0} = \frac{\Delta P_0 - \Delta P_x - (\pi_{BSA}^m - \pi_{BSA}^p) - (\pi_{DT10}^m - \pi_{DT10}^p)}{\mu_p R_m V_0} \quad (4.31)$$

where π^m and π^p represent, respectively, the osmotic pressure at the membrane surface and in the permeate flux, R_m the membrane resistance, ΔP_x the pressure drop along the membrane and μ_p the viscosity of the permeate flux.

The osmotic pressure, at both sides of the membrane, is function of the concentration of the solutes. This dependence is going to be expressed in terms of the rejection coefficients. Introducing the rejection coefficients – equation (4.2) – of both components, equation (4.31) becomes:

$$v_m = \frac{\Pi_{v_0}}{1 - (\Pi_{\pi_0})_{BSA} - (\Pi_{\pi_0})_{DT10}} \times \left\{ \begin{aligned} &1 - \frac{\Delta P_x}{\Delta P_0} - R_{BSA} (\Pi_{\pi_0})_{BSA} c_{BSA} - R_{DT10} (\Pi_{\pi_0})_{DT10} c_{DT10} + \\ &- [1 - (1 - R_{BSA})^2] (\Pi_{\pi_1})_{BSA} (\Pi_{\pi_0})_{BSA} c_{BSA}^2 + \\ &- [1 - (1 - R_{DT10})^2] (\Pi_{\pi_1})_{DT10} (\Pi_{\pi_0})_{DT10} c_{DT10}^2 + \\ &- [1 - (1 - R_{BSA})^3] (\Pi_{\pi_2})_{BSA} (\Pi_{\pi_0})_{BSA} c_{BSA}^3 + \\ &- [1 - (1 - R_{DT10})^3] (\Pi_{\pi_2})_{DT10} (\Pi_{\pi_0})_{DT10} c_{DT10}^3 \end{aligned} \right\} \quad (4.32)$$

where:

$$\Pi_{v_0} = \frac{\Delta P_0 - k_1^{BSA} C_0^{BSA} - k_1^{DT10} C_0^{DT10}}{\bar{\mu}_p^s R_m^s V_0} \quad (4.33)$$

$$(\Pi_{\pi_0})_{BSA} = \frac{k_1^{BSA} C_0^{BSA}}{\Delta P_0}; \quad (\Pi_{\pi_1})_{BSA} = \frac{k_2^{BSA} (C_0^{BSA})^2}{k_1^{BSA} C_0^{BSA}}; \quad (\Pi_{\pi_2})_{BSA} = \frac{k_3^{BSA} (C_0^{BSA})^3}{k_1^{BSA} C_0^{BSA}} \quad (4.34)$$

$$(\Pi_{\pi_0})_{DT10} = \frac{k_1^{DT10} C_0^{DT10}}{\Delta P_0}; \quad (\Pi_{\pi_1})_{DT10} = \frac{k_2^{DT10} (C_0^{DT10})^2}{k_1^{DT10} C_0^{DT10}}; \quad (\Pi_{\pi_2})_{DT10} = \frac{k_3^{DT10} (C_0^{DT10})^3}{k_1^{DT10} C_0^{DT10}} \quad (4.35)$$

The physical meaning of the dimensionless groups listed in the previous equations is described in detail by Miranda and Campos [31].

At the membrane surface, $v_m = -v_z(x, 0)$, and, for each component, the difference between the convective flux promoted by suction and the flux through the membrane is equal to the diffusive flux in the opposite direction promoted by the concentration gradient between the membrane surface and the bulk:

$$-\frac{1}{Pe_i} \frac{\partial c_i}{\partial z} = v_m (c_i^m - c_i^p) \quad (4.36)$$

or in terms of the rejection coefficients:

$$-\frac{1}{Pe_i} \frac{\partial c_i}{\partial z} = c_i^m v_m R_i \quad (4.37)$$

The rejection coefficient, R_i , depends on the hindrance transport across the membrane. The values of R_i are determined by equation (4.8) which presupposes hindrance transport of solute along the membrane pores. For the ϕ_i variable, equation (4.37) becomes:

$$-\frac{1}{Pe_i} \frac{\partial \phi_i}{\partial z} = v_m R_i \quad (4.38)$$

The derivative on the left hand side of the equation is approximated by a second order non-central difference and the concentration in the wall is determined explicitly in each time step.

All the boundary conditions at the membrane surface are represented in Table 4.7.

Table 4.7 - Boundary conditions at membrane surface for a generic component.

V
$v_x = 0$
Equation 4.32
$\psi = -\frac{1}{2} + \int -v_z dx$
$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$
$-\frac{1}{Pe_i} \frac{\partial c_i}{\partial z} = v_z c_i R_i$
$-\frac{1}{Pe_i} \frac{\partial \phi_i}{\partial z} = v_z R_i$

Sometimes along the work, to evaluate the performance of the separation process, it is necessary to define mean variables:

- The mean normalized solute concentrations at the membrane surface, $\bar{c}_{BSA}^m$ and $\bar{c}_{DT10}^m$,

$$\bar{c}_{BSA}^m = \frac{\int_0^{L_m} c_{BSA}^m(x, 0) dx}{\int_0^{L_m} dx}, \quad \bar{c}_{DT10}^m = \frac{\int_0^{L_m} c_{DT10}^m(x, 0) dx}{\int_0^{L_m} dx} \quad (4.39)$$

- The mean normalized velocity at the membrane surface,

$$\bar{v}_m = \frac{\int_0^{L_m} v_z(x, 0) dx}{\int_0^{L_m} dx} \quad (4.40)$$

where x is the normalized longitudinal coordinate with origin at the beginning of the membrane.

The mean selectivity, real or apparent, is defined taking the mean concentration values.

4.3.8. Convergence

The study of the convergence of the numerical method was based on the residues of the vorticity equation and on the evolution of the error in the concentration of the solutes in a critical node of the cell. The critical node is one of the nodes where the convergence is slower: at the membrane surface and near the cell exit and it was chosen by simple inspection.

The residues of the vorticity equation, R_ω , were determined by:

$$R_\omega = \sum_{i=2}^{n-1} \sum_{j=2}^{m-1} \left| \frac{\partial \omega}{\partial t} \right|_{i,j} \quad (4.41)$$

where $\left| \frac{\partial \omega}{\partial t} \right|_{i,j}$ is the time derivative of the vorticity at the node (i, j) .

The error of the concentration in the critical node was determined by:

$$\mathcal{E}_{crit} = \left| \frac{c_{crit}^k - c_{crit}^{k-1}}{c_{crit}^k} \right| \quad (4.42)$$

where *crit* refers to the critical node and k to the current iteration.

An example of the study of the convergence is presented in Figure 4.4. The normalized concentration converges to a constant value, and the residues of the vorticity equation decrease to very small values. The iterative process stops when the following criterions were observed:

$$\begin{cases} \mathcal{E}_{crit} < 10^{-7} \\ R_\omega < 10^{-2} \end{cases} \quad (4.43)$$

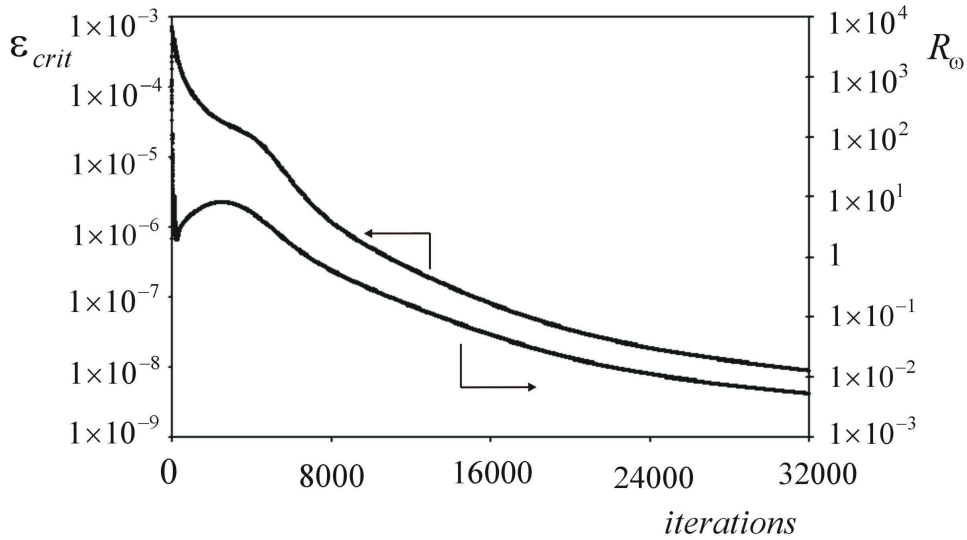


Figure 4.4 - Residues of the vorticity equation and error of the concentration of BSA at a critical

node versus the number of iterations ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$; $Re_0 = 1387$; $V_0 = 1.632$;

$$Pe_{BSA}^0 = 2.36 \times 10^7; \Delta P_0 = 2.43 \times 10^5 \text{ Pa}).$$

4.4. Results and discussion

4.4.1. Mean real and apparent selectivities

Figure 4.5 shows how the mean selectivities (real and apparent) change with the transmembrane pressure applied. The data is for low inlet solute concentrations and laminar flow. Curves obtained neglecting the pressure drop along the cell and including the pressure drop are both represented.

The real mean selectivity increases with increasing transmembrane pressure, until the curve converges asymptotically to a constant value. According to equations (4.3) and (4.7), this asymptotic value is:

$$\sigma = \frac{S_{i,\infty}}{S_{j,\infty}} = 5 \quad (4.44)$$

with the asymptotic intrinsic sieving coefficients calculated by equations (4.9-4.11).

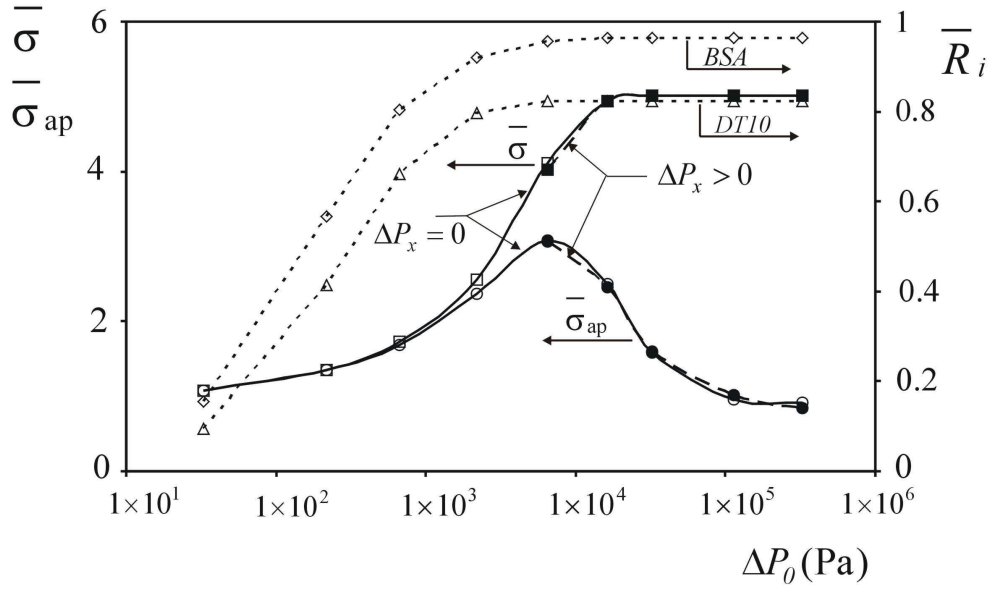


Figure 4.5 – Mean real selectivity, mean apparent selectivity and mean rejection of BSA and Dextran-T10 versus transmembrane pressure for $Re_0 = 60$ ($V_0 = 0.057\text{m/s}$), $C_{BSA}^0 = 0.05\text{ kg/m}^3$, $C_{DT10}^0 = 0.05\text{ kg/m}^3$, $Pe_{BSA}^0 = 8.18 \times 10^5$ and $Pe_{DT10}^0 = 5.46 \times 10^5$.

If the pressure drop is neglected, the mean apparent selectivity increases with increasing transmembrane pressure until a maximum and then decreases converging to a constant value. The maximum is related to the attainment of the asymptotic intrinsic sieving coefficient of the solutes (Figure 4.5). After this attainment, the concentration of the solutes in the permeate flux becomes only determined by the respective concentrations over the membrane. The rate of accumulation of BSA is higher than that of Dextran-T10 (higher asymptotic intrinsic sieving coefficient and lower molecular diffusivity) and so the apparent selectivity decreases.

However, the cell is too long and, consequently, the pressure drop is too high to be neglected. If the pressure drop is taken into account, the pressure range, for which the operation is possible, shrinks. For low transmembrane pressures at the cell inlet, the effective transmembrane pressure along the membrane becomes negative. Data points shown in Figure 4.5 are those for which the effective transmembrane pressure is positive at the end of the cell.

The data of the mean apparent selectivity in Figure 4.5 are, obviously, dependent on the length of the membrane. Taking the value of the transmembrane pressure for the highest

mean selectivity of the previous example, the mean apparent selective was successively calculated for several membrane lengths. The data in Figure 4.6 show a slow decrease of the selectivity with the length of the membrane.

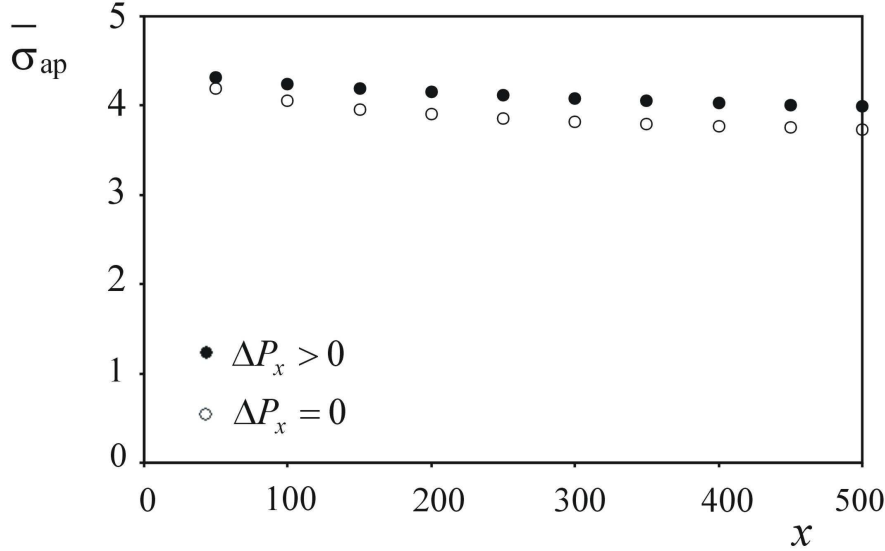


Figure 4.6 – Mean apparent selectivity versus normalized membrane length for $Re_0 = 1387$

($V_0 = 1.324 \text{ m/s}$), $C_{BSA}^0 = 0.05 \text{ kg/m}^3$, $C_{DT10}^0 = 0.05 \text{ kg/m}^3$, $Pe_{BSA}^0 = 1.89 \times 10^7$, $Pe_{DT10}^0 = 1.26 \times 10^7$
and $\Delta P_0 = 1.01 \times 10^4 \text{ Pa}$.

4.4.2. Mean apparent selectivity versus inlet Reynolds number

Figure 4.7 shows the mean apparent selectivity data for different inlet Reynolds numbers (same inlet concentrations and membrane length). The results were obtained by taking into account the pressure drop along the cell. The effective transmembrane pressure is positive in every point along the cell only for high ΔP_0 . For the highest transmembrane pressures, all the curves tend asymptotically to 1.

The mean apparent selectivity increases with increasing Reynolds number. This increase is a consequence of a polarization decrease: when the tangential convection increases, the concentration of the components at the membrane surface decreases. This effect is higher for the component with the lower transmission, i.e., BSA. For this reason, the transmission of BSA decreases more than the transmission of Dextran-T10 and, consequently, the selectivity increases. These results are consistent with experimental data from the literature [4-10],

which show a decrease in transmission and an increase in selectivity with decreasing polarization.

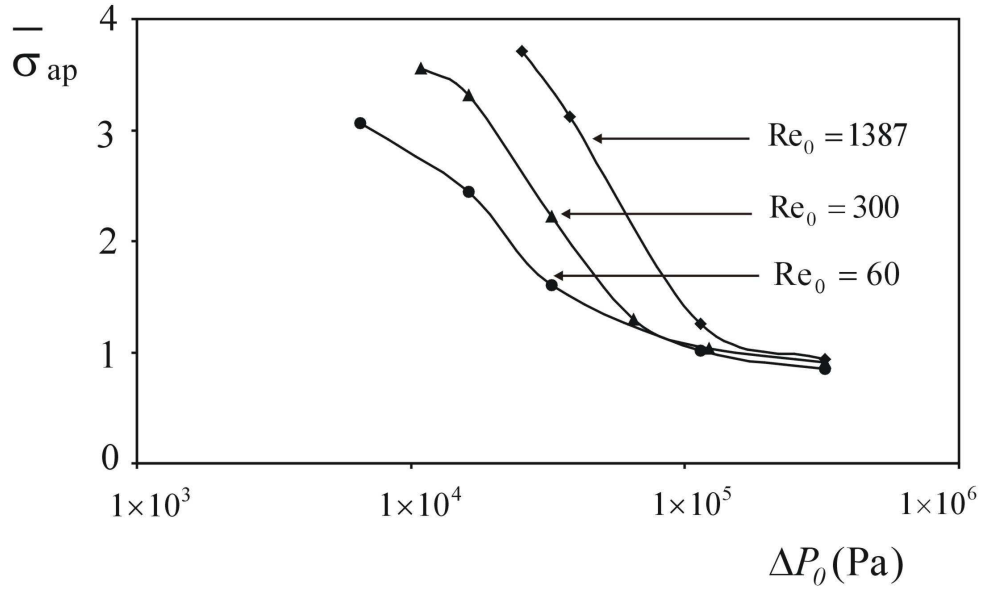


Figure 4.7 – Mean apparent selectivity versus transmembrane pressure for different inlet Reynolds numbers: $Re_0 = 60$ ($V_0 = 0.057\text{m/s}$, $Pe_{BSA}^0 = 8.18 \times 10^5$, $Pe_{DT10}^0 = 5.46 \times 10^5$), $Re_0 = 300$ ($V_0 = 0.286\text{m/s}$, $Pe_{BSA}^0 = 4.09 \times 10^6$, $Pe_{DT10}^0 = 2.73 \times 10^6$) and $Re_0 = 1387$ ($V_0 = 1.324\text{m/s}$, $Pe_{BSA}^0 = 1.89 \times 10^7$, $Pe_{DT10}^0 = 1.26 \times 10^7$) and for $\Delta P_x > 0$. The inlet concentrations are $C_{BSA}^0 = 0.05\text{ kg/m}^3$ and $C_{DT10}^0 = 0.05\text{ kg/m}^3$.

4.4.3. Mean apparent selectivity versus inlet solute concentrations

Figure 4.8 shows the same data of Figure 4.7 but for much higher solute inlet concentrations, $C_{BSA}^0 = 24.4\text{ kg/m}^3$ and $C_{DT10}^0 = 24.4\text{ kg/m}^3$. Comparing the data of both figures, the mean apparent selectivity depends on the inlet concentration of the solutes: for increasing inlet concentration values, the mean apparent selectivity curve suffers a translation along the transmembrane pressure axis and simultaneously a compression. The translation is a consequence of the increase of the osmotic pressure over the membrane and by consequence of the decrease of the real pressure driving force. It should be stressed the narrow transmembrane pressure range where fractionation happens.

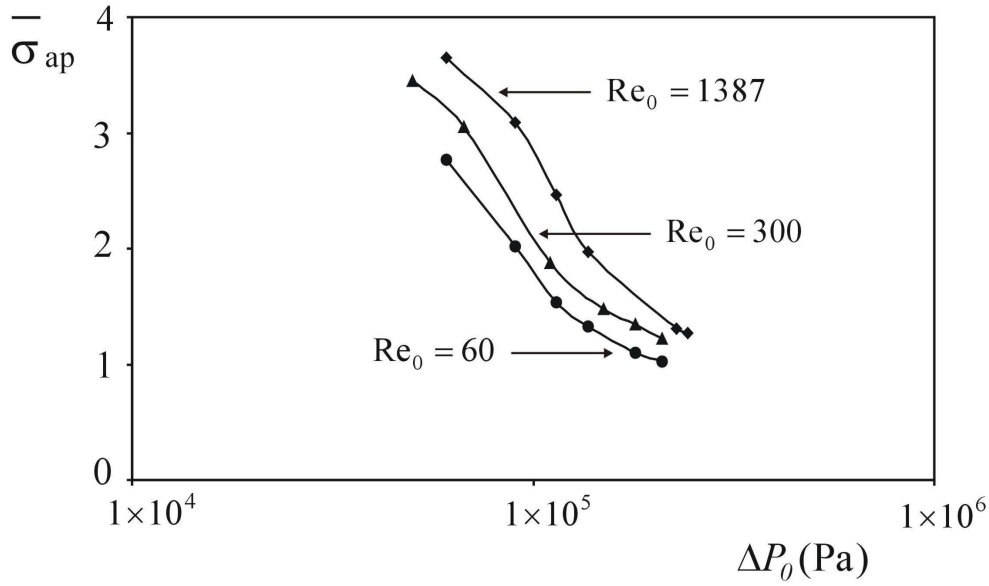


Figure 4.8 – Mean apparent selectivity versus transmembrane pressure for highly concentrated solutions ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$ and $C_{DT10}^0 = 24.4 \text{ kg/m}^3$) and different inlet Reynolds numbers: $Re_0 = 60$ ($V_0 = 0.071 \text{ m/s}$, $Pe_{BSA}^0 = 1.02 \times 10^6$, $Pe_{DT10}^0 = 6.72 \times 10^5$), $Re_0 = 300$ ($V_0 = 0.353 \text{ m/s}$, $Pe_{BSA}^0 = 5.12 \times 10^6$, $Pe_{DT10}^0 = 3.36 \times 10^6$) and $Re_0 = 1387$ ($V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$) and for $\Delta P_x > 0$.

4.4.4. Selectivity and polarization

An increase of the transmembrane pressure leads to an increase of the permeate velocity, which promotes the accumulation of solute near the membrane, i. e., the concentration polarization of the membrane (figures 4.5-4.8). The effect is more pronounced for the component with higher rejection, which is also the component with lower diffusivity. As shown in Figure 4.9a, the concentrations of both solutes increase, but the slope of the curve is higher for BSA. For high permeate velocities, the rejection of the components becomes constant (Figure 4.5) and so, the concentrations in the permeate become proportional to the concentrations at the membrane surface. An increase of the surface concentrations induces a proportional increase of the permeate concentrations (Figure 4.9), i.e., the transmission of each solute increases proportionally. This increase is more significant for BSA, and for this reason the selectivity decreases with polarization increase (Figure 4.8). The results obtained here are consistent with the results reported in the literature [4-10].

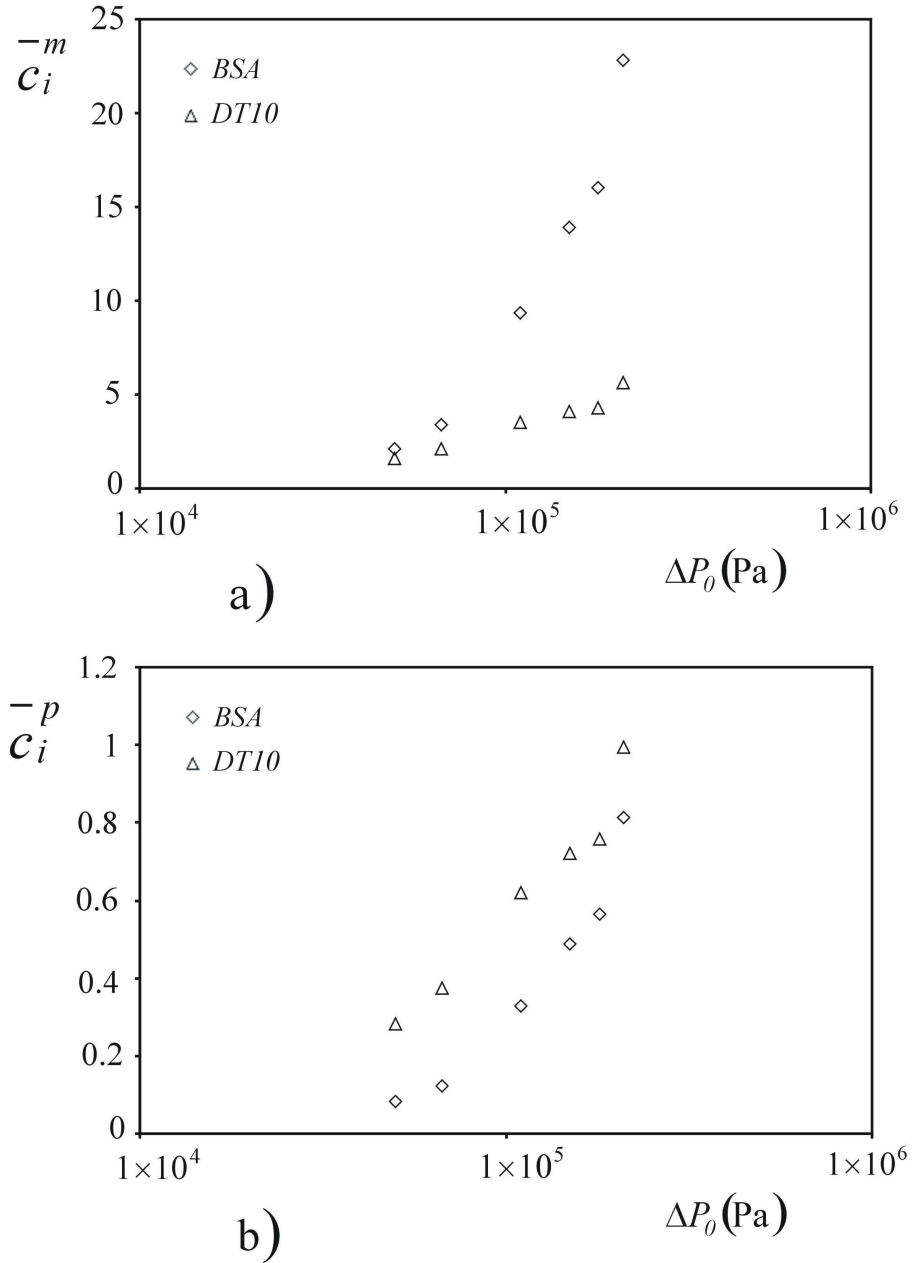


Figure 4.9 – Mean normalized concentration of BSA and Dextran-T10, versus transmembrane pressure: a) at membrane surface; b) in the permeate stream, for $Re_0 = 300$ ($V_0 = 0.353\text{m/s}$), $C_{BSA}^0 = 24.4\text{kg/m}^3$ and $C_{DT10}^0 = 24.4\text{kg/m}^3$, $Pe_{BSA}^0 = 5.12 \times 10^6$, $Pe_{DT10}^0 = 3.36 \times 10^6$ and $\Delta P_x > 0$.

4.4.5. Effect of the pore size and membrane resistance

The transmission of the solutes across the membrane, determined by the convection-diffusion model, is based on the theory of hindered transport of solutes in the pores. Particles and molecules diffuse/convect at a slow velocity inside pores with a size similar to that of the particles/molecules. The hindered transport is determined by the pores size and geometry

and by the diameter of the solutes. So, different membranes will have different selectivities. Additionally, the permeate flow velocity, which affects concentration polarization, depends on the membrane resistance. To study these effects, simulations for different pore sizes and different membrane resistances were performed.

Figure 4.10 shows the effect of the variation of the specific area of the pores of the membrane. For a given transmembrane pressure, the selectivity curve has an asymptote, a value of s for which the selectivity is very high, decreasing from this value on with the increase of the specific area of the pores. This increase of the pore size leads to a decrease in selectivity because the rejection of BSA decreases while the rejection of Dextran-T10 is unaffected. For large pores the selectivity becomes insensitive to changes in the transmembrane pressure. To the left side of the asymptote, the selectivity is not defined because the BSA is completely rejected.

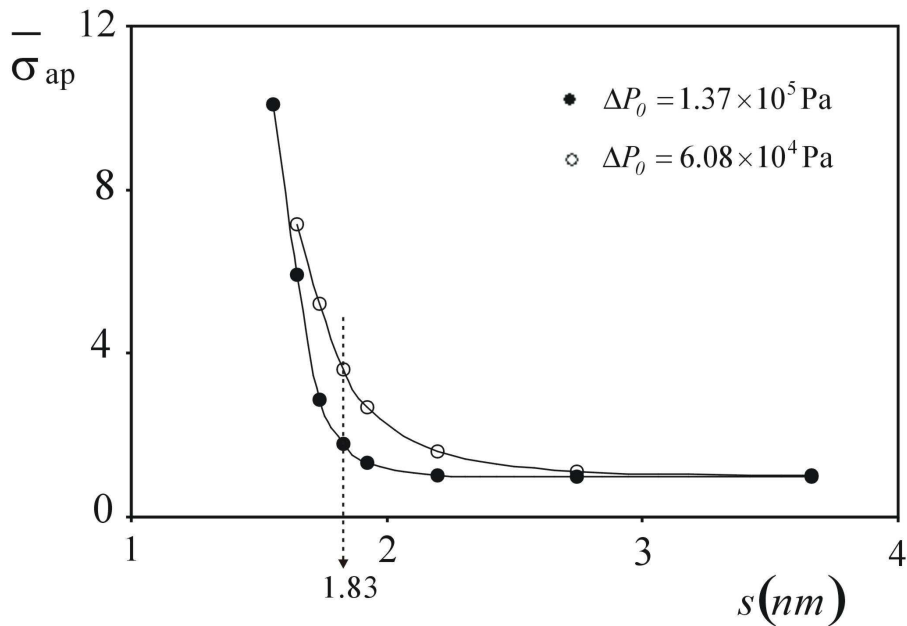


Figure 4.10 - Mean apparent selectivity versus specific area of the pores of the membrane for two values of transmembrane pressure: $\Delta P_0 = 1.37 \times 10^5$ Pa and $\Delta P_0 = 6.08 \times 10^4$ Pa ($C_{BSA}^0 = 24.4$ kg/m³ and $C_{DT10}^0 = 24.4$ kg/m³, $Re_0 = 1387$, $V_0 = 1.632$ m/s, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$) and for $\Delta P_x > 0$.

Figure 4.11 shows the selectivity as function of the membrane resistance for two values of the transmembrane pressure. For increasing membrane resistances, the permeate velocity

decreases and, consequently, the polarization of the membrane also decreases. Therefore, for each transmembrane pressure, the selectivity increases with the membrane resistance.

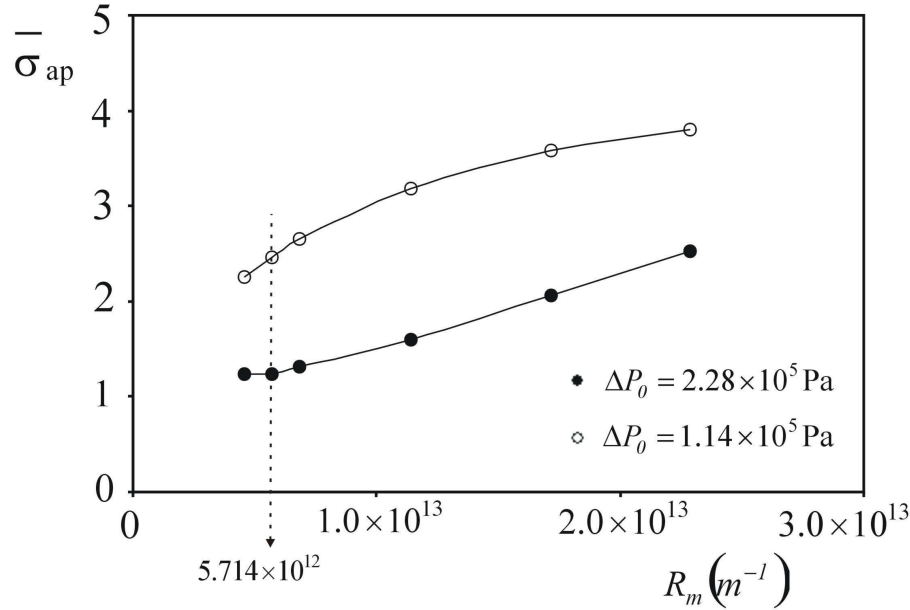


Figure 4.11 - Mean apparent selectivity versus membrane resistance for two values of transmembrane pressure: $\Delta P_0 = 2.28 \times 10^5$ Pa and $\Delta P_0 = 1.14 \times 10^5$ Pa ($C_{BSA}^0 = 24.4$ kg/m³ and $C_{DT10}^0 = 24.4$ kg/m³, $Re_0 = 1387$, $V_0 = 1.632$ m/s, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$) and for $\Delta P_x > 0$.

4.4.6. The effect of the variation of the physical properties on the apparent selectivity

The effect of the variation of the physical properties, viscosity of the solution and molecular diffusion of the solutes, on the apparent selectivity was also analysed. For diluted inlet solutions ($C_{BSA}^0 = 0.05$ kg/m³ and $C_{DT10}^0 = 0.05$ kg/m³), and for the range of conditions studied, this effect is not appreciable (Figure 4.12a). For concentrated inlet solutions ($C_{BSA}^0 = 24.4$ kg/m³ and $C_{DT10}^0 = 24.4$ kg/m³), it is observed a decrease in the selectivity when the variation of the physical properties are taken into account (Figure 4.12b). For the latter conditions, a comparison between the concentrations along the membrane and between the permeate velocities is shown in Figures 4.13 and 4.14. Figure 4.13 shows that the concentration of BSA is higher when variable transport properties are considered. This behaviour is justified by: (i) a decrease of the diffusivity of BSA with concentration; (ii) a

decrease of the tangential velocity due to the increase of solution viscosity. The same effect is smaller in the concentration of Dextran-T10 because its diffusivity is concentration independent and the level of polarization is lower and, consequently, less sensitive to changes in the velocity profile.

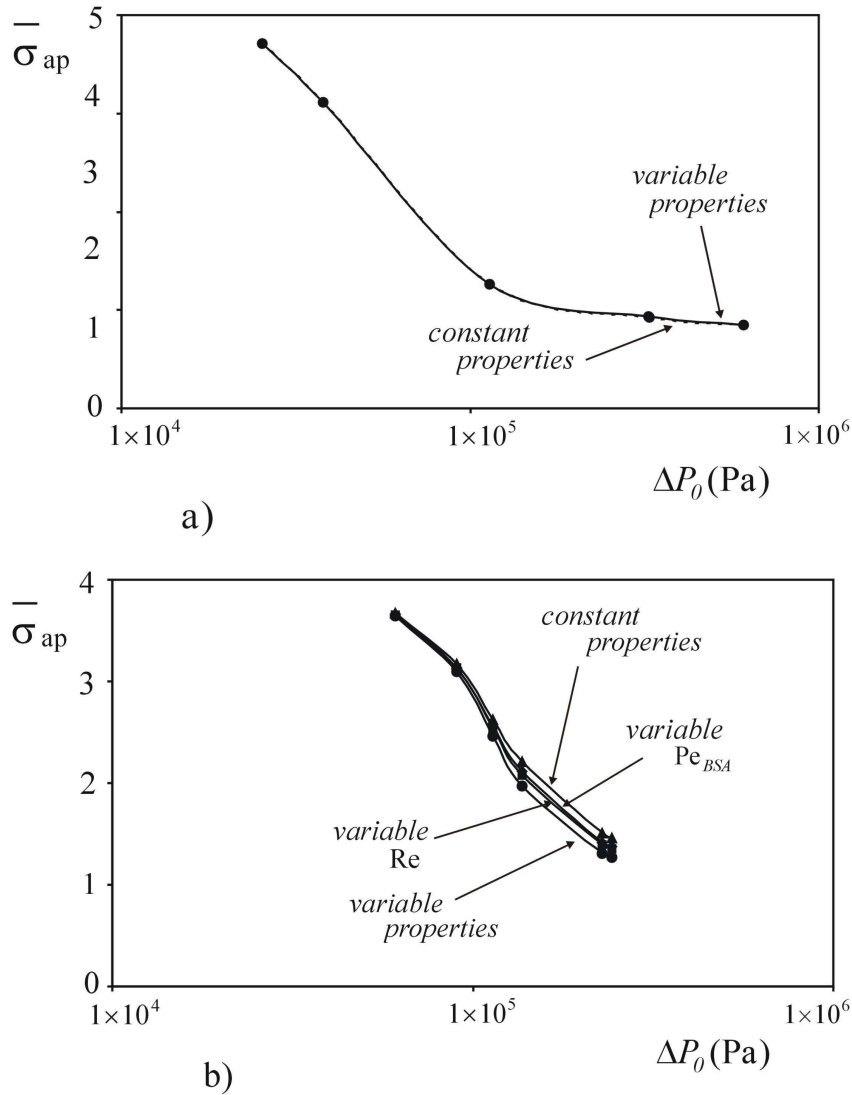


Figure 4.12 – Effect of concentration dependent properties in the apparent selectivity versus transmembrane pressure: (a) low inlet concentrations ($C_{BSA}^0 = 0.05 \text{ kg/m}^3$, $C_{DT10}^0 = 0.05 \text{ kg/m}^3$), $Re_0 = 1387$ ($V_0 = 1.324 \text{ m/s}$), $Pe_{BSA}^0 = 1.89 \times 10^7$ and $Pe_{DT10}^0 = 1.26 \times 10^7$; (b) high inlet concentrations ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$), $Re_0 = 1387$ ($V_0 = 1.632 \text{ m/s}$), $Pe_{BSA}^0 = 2.36 \times 10^7$ and $Pe_{DT10}^0 = 1.55 \times 10^7$, both for $\Delta P_x > 0$.

In Figure 4.12b are also plotted the curve for constant Reynolds number (constant solution viscosity) and variable Peclet numbers and the curve for variable Reynolds number

and constant Peclet numbers. The curves are practically coincident and they are located between the curve of variable properties and the curve of constant properties, meaning that the variation of the Reynolds number and the variation of the Peclet numbers, both with concentration, have the same contribution to the decrease of the selectivity. However, this decrease is not very significant. This low sensitivity is in accordance with the data of Shen and Probstein [15].

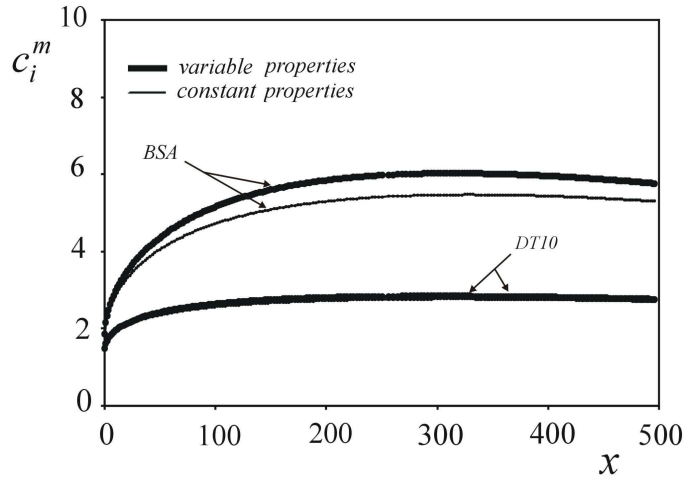


Figure 4.13 – Effect of concentration dependent properties in the concentration profiles along the membrane surface for $Re_0 = 1387$ ($V_0 = 1.632\text{m/s}$), $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $C_{BSA}^0 = 24.4\text{kg/m}^3$, $C_{DT10}^0 = 24.4\text{kg/m}^3$, $\Delta P_0 = 1.14 \times 10^5$ and for $\Delta P_x > 0$.

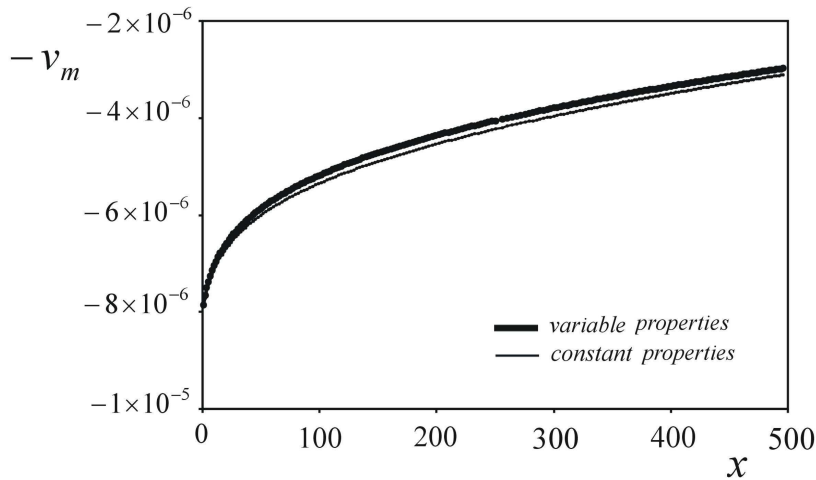


Figure 4.14 – Effect of concentration dependent properties in the permeate velocity profile along the membrane surface for $Re_0 = 1387$ ($V_0 = 1.632\text{m/s}$), $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $C_{BSA}^0 = 24.4\text{kg/m}^3$, $C_{DT10}^0 = 24.4\text{kg/m}^3$, $\Delta P_0 = 1.14 \times 10^5$ and for $\Delta P_x > 0$.

4.5. Conclusions

The apparent selectivity in the fractionation of BSA and Dextran-T10 was studied by numerical methods, CFD. By coupling the flow and mass transport equations with a convective-diffusive model for the transport of solutes through the membrane, it was possible to predict by the apparent selectivity of the process. The variation of diffusivity and viscosity with the concentration of the solutes was taken into account. By following a numerical approach, it was possible to relate in detail the concentration polarization of the membrane, the transmission of each component and the apparent selectivity.

When the pressure drop along the cell is negligible, the mean apparent selectivity increases with increasing transmembrane pressures until it reaches a maximum after which decreases. The apparent selectivity increases in the first half of the curve due to the increase of transmission by convection and decreases in the second half due to concentration polarization. When the pressure drop along the cell is significant, the first half of the apparent selectivity curve cannot be observed because the transmembrane pressure is negative in parts of the cell.

The mean apparent selectivity increases with increasing Reynolds number, consequence of a decrease of the concentration polarization. For a given transmembrane pressure, the selectivity increases with a decrease of the area of the membrane pores and also with an increase of the resistance of the membrane.

For low inlet concentrations of the solutes, the variation of the physical properties with the concentration does not produce any appreciable effect on the apparent selectivity. For high inlet concentrations, and appreciable transmembrane pressures, the apparent selectivity is lower when the effect of the variation of the physical properties with concentration is taken into account. The effect of the variation of the physical properties is mainly due to the variations of molecular diffusivity of BSA and viscosity of the solution with concentration.

While, in the present work, solute-solute interactions and solute-membrane interactions were not taken into account, these interactions are an important factor to quantify the selectivity. In future works, these interactions will be studied.

4.6. Nomenclature

C_i	Concentration of component i
c_i	Normalized concentration of component i
C_i^0	Concentration of component i at the feed stream
C_i^m	Concentration of component i at membrane surface
c_i^m	Normalized concentration of component i at membrane surface
$\overline{C}_i^m$	Mean concentration of component i at membrane surface
$\overline{c}_i^m$	Mean normalized concentration of component i at membrane surface
C_i^p	Permeate concentration of component i
c_i^p	Normalized permeate concentration of component i
$\overline{C}_i^p$	Mean permeate concentration of component i
$\overline{c}_i^p$	Mean normalized permeate concentration of component i
$\overline{c}_i^{m,ref}$	Mean normalized reference concentration of component i at membrane surface
c_{crit}^k	Normalized concentration on a critical location at a current iteration k
D_i	Molecular diffusivity of component i
$D_{i,\infty}$	Free diffusivity of component i
$D_{i,eff}$	Effective diffusivity of component i
d_h	Hydraulic diameter
H	Distance between parallel plates
K_i^c	Factor of convective transport of component i
K_i^d	Factor of diffusive transport of component i
k	Current time step
k_1^i	First virial coefficient for component i
k_2^i	Second virial coefficient for component i
k_3^i	Third virial coefficient for component i
L_{out}	Length of the outlet section

L_{in}	Length of the inlet section
L_m	Total length of the membrane
L	Length of the cell
m	Number of vertical nodes
n	Number of horizontal nodes
N_i	Total flux of component i
ni_m	Number of longitudinal nodes at membrane surface
P	Pressure
p	Normalized pressure
p_0	Normalized reference pressure
R_i	Real rejection of component i
$\overline{R}_i$	Mean rejection of component i
r_i^*	Equivalent molecular radius of component i
R_m	Membrane resistance
R_ω	Residual of the vorticity equation
S	Equation 4.25
S_i	True sieving coefficient of component i
S_{ap_i}	Apparent sieving coefficient of component i
$S_{i,\infty}$	Asymptotic intrinsic sieving coefficient of component i
s	Specific area of the pores
t	Time
V_0	Mean feed velocity
V_m	Permeate velocity
v_m	Normalized permeate velocity
$\overline{V}_m$	Mean permeate velocity
$\overline{v}_m$	Mean normalized permeate velocity
V_x	Longitudinal component of the velocity
v_x	Normalized longitudinal component of the velocity
V_z	Vertical component of the velocity
v_z	Normalized vertical component of the velocity
X	Longitudinal coordinate

ΔX	Distance between two consecutive horizontal nodes
x	Normalized longitudinal coordinate
x_i	Mass fraction of component i
Z	Vertical coordinate
ΔZ	Distance between two consecutive vertical nodes
z	Normalized vertical coordinate
W	Width of the cell

Non-dimensional numbers

Eu_0	Euler number
Pe_i	Peclet number of component i
Pe_i^0	Peclet number of component i at the feed stream
Re	Reynolds number
Re_0	Reynolds number at the feed stream
Π_{v_0}	Equation 4.33
$(\Pi_{\pi_0})_i$	Equations 4.34 and 4.35
$(\Pi_{\pi_1})_i$	Equations 4.34 and 4.35
$(\Pi_{\pi_2})_i$	Equations 4.34 and 4.35

Greek Symbols

ΔP_0	Static pressure difference across the membrane
ΔP_x	Pressure drop along the membrane
ε_{ci}^{-m}	Numerical error of the concentration of the component i at the membrane surface
ε_{crit}	Numerical error on a critical location
π_i	Osmotic pressure of component i
π_i^m	Osmotic pressure of component i at the membrane surface
π_i^p	Osmotic pressure of component i in the permeate flux

$\Delta\pi_i$	Contribution of component i to the osmotic pressure difference across the membrane
ψ	Stream function
ω	Vorticity
ρ	Density
μ	Viscosity
$\bar{\mu}$	Mean viscosity
μ_i	Viscosity of a solution of component i
μ_p	Viscosity of the permeate stream
ϕ_i	$\ln(c_i)$
ϕ_i^p	Constant of proportionality representing the equilibrium partition coefficient
σ_{ap}	Apparent selectivity
$\bar{\sigma}_{ap}$	Mean apparent selectivity
σ	Real selectivity
$\bar{\sigma}$	Mean real selectivity
δ_m	Membrane thickness
λ_i	Constant which depends on the equivalent molecular radius of component i

4.7. References

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Chapter 5

Use of hybrid membrane cells to improve the apparent selectivity in the fractionation of two components – CFD study

The fractionation of aqueous solutions of BSA and Dextran-T10 in a Hybrid Membrane Cell is studied by numerical methods. The Hybrid Membrane Cell has n semi-permeable and n fully-permeable membrane sub-sections alternating in series. The cell has a feed stream and three outlet streams: the retentate stream, a BSA-rich permeate stream and a Dextran-rich permeate stream. The flow and concentration fields of the solutes are determined by solving the Navier-Stokes and the mass transport equations. The apparent selectivity of the separation process is determined from the concentrations of the solutes in the permeate streams.

The selectivity of a Hybrid Membrane Cell is compared with the selectivity of a conventional membrane cell. The selectivity is higher in the Hybrid Membrane Cell due to the depolarization effect promoted by the fully-permeable membranes. The difference is significant in the range of transmembrane pressure for which the membrane of the conventional cell becomes polarized. The selectivity of the Hybrid Membrane Cell is maximized for high permeate velocities through the fully-permeable membranes and high number of membrane sections. Additionally, the less transmitted component is preferentially recovered in the stream that crosses the fully-permeable membranes. In comparison with conventional cells, the Hybrid Membrane Cell has good performance along a large range of the transmembrane pressure, a characteristic that gives it a good operational flexibility.

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5.1. Introduction

Fractionation of macromolecules in aqueous solutions is a common problem in the food, biotechnological and pharmaceutical industries. One approach to this problem is to combine a high productivity process, in order to concentrate the macromolecules and to reduce the volume of the feed stream, with a high selectivity process, dedicated to the purification/fractionation of the desired macromolecules [1].

Membrane ultrafiltration is a promising process to fractionate macromolecules because it has the potential to be simultaneously a high productivity and a high selectivity process. In fractionation by ultrafiltration, one of the solutes permeates the membrane and is recovered in the permeate stream, while the other is rejected by the membrane and is recovered in the retentate stream. The productivity of an ultrafiltration process is high, but the selectivity can be limited by several factors, such as broad pore size distribution [1, 2], physicochemical conditions [3-5] and concentration polarization [6-8]. To achieve a high selectivity and to make protein fractionation commercially viable, several research groups [9-11] developed high performance approaches to fractionation by ultrafiltration. These approaches are based on the selection of membranes with a narrow pore size distribution and appropriate electrical charge to maximize selectivity and on the selection of flow conditions to minimize concentration polarization.

Experimental results show that the concentrated layer over a membrane induced by permeation, i.e. polarisation phenomena, increases the transmission of the macromolecules [6-8, 12-14]. Since this effect is higher for the macromolecule with the lowest transmission, concentration polarization usually contributes to reduce the selectivity of macromolecules fractionation by ultrafiltration [6-8].

High performance approaches require the development of methods to reduce concentration polarization. Several methods have been proposed to reduce polarization [15], including Dean vortices [13, 16], oscillatory flows [17-21], flow enhanced by Taylor bubbles [7,8], turbulence promoters [22] and Hybrid Membrane Cells [23, 24]. Backflushing [25-28] is mainly a method to remove fouling and pore blocking of ultrafiltration and microfiltration membranes, but is also useful to reduce concentration polarization.

Hybrid Membrane Cells are cells which have membranes of different properties (e.g. semi-permeable and fully-permeable membranes) alternating along the flow direction. This concept was applied by Miranda and Campos [23] to separate a feed stream with one solute into two parts: a solvent stream crossing the semi-permeable membranes and a concentrate stream crossing the fully-permeable membranes. The authors showed that the lower concentration polarization obtained in Hybrid Membrane Cells than in conventional cells was due to the cleaning effect on the mass boundary layer over the semi-permeable membranes. Pinto et al. [24] studied a new membrane fractionation process based on the combination of Hybrid Membrane Cells with the differential diffusion of two solutes. The semi-permeable membranes were permeable to the solvent and impermeable to both solutes, and the fully-permeable membranes were permeable to all components of the solution. The solute with the lower diffusivity accumulated preferentially over the surface of the semi-permeable membranes, and it was preferentially removed in the fully-permeable subsections. The retentate stream was then richer in the solute with the higher diffusivity.

The purpose of the present study is to analyse if a Hybrid Membrane Cell can significantly improve the selectivity of a fractionation process by ultrafiltration. The separation of two solutes (bovine serum albumin (BSA) and Dextran-T10) by a Hybrid Membrane Cell is studied by numerical methods. The Hybrid Membrane Cell has, alternating in series, semi-permeable membranes permeable to the solvent and partially permeable to both solutes and fully-permeable membranes permeable to all components. The flow and concentration fields in the membrane are determined by solving the mass transport and the Navier-Stokes equations coupled through a convective-diffusive transport model for the transmission of the solutes across the membrane [29].

5.2. Cell description

Figure 5.1 shows a schematic representation of a Hybrid Membrane Cell (more details in Miranda and Campos [23] and Pinto et al. [24]). Succinctly, the cell is a parallel plate with semi-permeable and fully-permeable membranes alternating in series along the walls. The semi-permeable membranes are permeable to the solvent and partially reject Dextran-T10 and BSA. These membranes are selective; the rejection of BSA is higher than that of Dextran-T10. The fully-permeable membranes are completely permeable to all components.

According to the layout, the cell has a feed stream and three outlet streams: 1- a Dextran-rich stream which crosses the semi-permeable membranes; 2- a BSA-rich stream which crosses the fully-permeable membranes; 3- a retentate stream.

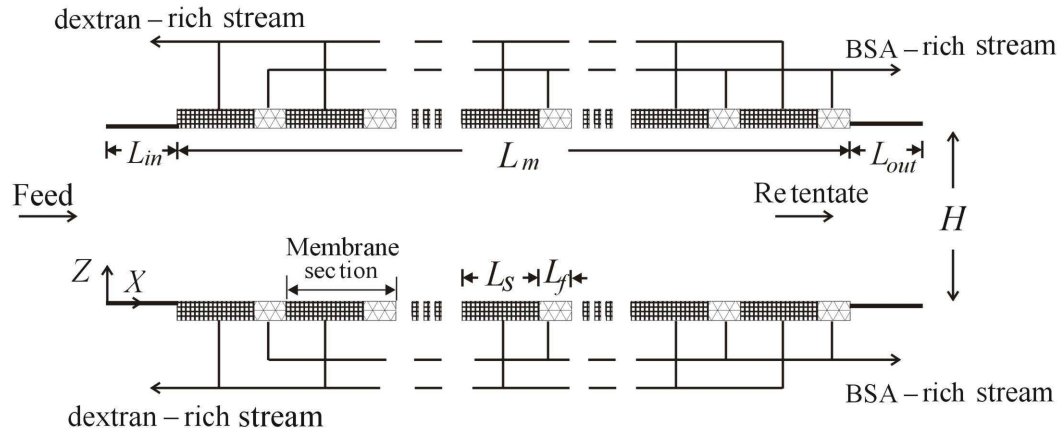


Figure 5.1 – Schematic representation of the Hybrid Membrane Cell.

In the schematic representation of Figure 5.1, H is the height of the cell (distance between the walls of the cell). The cell is divided into several sections: the inlet section (L_{in}), the outlet section (L_{out}) and n membrane sections (L_m). The total length of the cell is L . The inlet and outlet sections are both impermeable to the solutes and to the solvent. Each membrane section is composed by a semi-permeable membrane sub-section (L_s) and a fully-permeable sub-section (L_f).

The type of membrane used in the semi-permeable sub-section, the molecular weights of the solutes, and the cell dimensions are listed in Table 5.1.

Table 5.1 - Characteristics of the Hybrid Membrane Cell*

Membrane	Polysulfone membrane
MWCO	50 kDa
R_m^s	$5.714 \times 10^{12} \text{ m}^{-1}$
H	0.001 m
L_m	0.50 m

* Membrane and cell dimensions identical to those of Ghosh and Cui [8].

The performance of the Hybrid Membrane Cell will be compared with the performance of a conventional cell. The characteristics of the conventional cell are similar to those in Table 5.1, except that the conventional cell has only one semi-permeable membrane section with a length equal to the total length of the semi-permeable membranes of the Hybrid Membrane Cell. In the Hybrid Membrane Cell the fraction of the fully-permeable membrane area is:

$$\varepsilon = \frac{L_f}{L_s + L_f} \quad (5.1)$$

Along the study, all the uppercase variables will be dimensional variables and the lowercase variables are normalised variables. The concentrations are normalized by the inlet solute concentration, the velocities by the inlet mean velocity and the geometric dimensions by the height of the cell (H).

5.3. Numerical method

The apparent selectivity (σ_{ap}) is by definition:

$$\sigma_{ap} = \frac{S_{ap_i}}{S_{ap_j}} = \frac{C_i^p / C_i^b}{C_j^p / C_j^b} \quad (5.2)$$

where S_{ap_i} and S_{ap_j} represent the apparent sieving coefficients, defined by the ratio between the concentration of a solute in the permeate, C_i^p or C_j^p , and that in the bulk, C_i^b or C_j^b . The index i symbolizes the preferentially transmitted solute (Dextran-T10) and j symbolizes the preferentially rejected solute (BSA).

5.3.1. Conservative equations

The flow and the concentration fields in Hybrid Membrane Cells were studied by solving the conservative flow and mass transport equations. The flow field was determined by solving the Navier-Stokes equations written in the stream function–vorticity formulation

$(\psi - \omega)$ and Cartesian coordinates (x and z) with variable physical properties [30]. The flow is characterized by the Reynolds number based on the mean inlet velocity and height of the cell:

$$\text{Re} = \frac{\rho V_0 H}{\bar{\mu}} \quad (5.3)$$

where ρ is the fluid density and $\bar{\mu}$ is the viscosity of the mixture.

The dimensionless mass transport equation for component i is:

$$\frac{\partial c_i}{\partial t} + v_x \frac{\partial c_i}{\partial x} + v_z \frac{\partial c_i}{\partial z} = \frac{\partial \left(\frac{1}{\text{Pe}_i} \frac{\partial c_i}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{1}{\text{Pe}_i} \frac{\partial c_i}{\partial z} \right)}{\partial z} \quad (5.4)$$

where t is the non-dimensional time, c_i is the normalized concentration of component i and Pe_i the respective Peclet number:

$$\text{Pe}_i = \frac{V_0 H}{D_i} \quad (5.5)$$

where D_i is the molecular diffusivity of component i .

The mass transport equation was solved by the so-called ϕ method [31]. In this method, a variable transformation $\phi = \ln(c_i)$ is used to linearize the concentration gradients in the mass boundary layer over the membrane. The mass transport equation is then converted into the ϕ transport equation:

$$\frac{\partial \phi_i}{\partial t} + \left(v_x - \frac{\partial}{\partial x} \frac{1}{\text{Pe}_i} - \frac{1}{\text{Pe}_i} \frac{\partial \phi_i}{\partial x} \right) \frac{\partial \phi_i}{\partial x} + \left(v_z - \frac{\partial}{\partial z} \frac{1}{\text{Pe}_i} - \frac{1}{\text{Pe}_i} \frac{\partial \phi_i}{\partial z} \right) \frac{\partial \phi_i}{\partial z} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 \phi_i}{\partial x^2} + \frac{\partial^2 \phi_i}{\partial z^2} \right) \quad (5.6)$$

The equations were discretized by a finite difference method (more details about the discretization method and the numerical solution of the discretized equations are in Afonso et al. [30] and Miranda and Campos [23, 31]).

5.3.2. Physical properties

Concentration dependent transport properties (viscosity of the solution and diffusivity of the solutes) and a non-linear concentration dependent osmotic pressure were considered.

The feed stream studied is an aqueous solution containing dissolved molecules of BSA and Dextran-T10 with pH = 4.7 and ionic strength of 0.15 M (BSA isoelectric point). Dextrans are complex polysaccharides made of many glucose molecules, available in multiple molecular weights ranging from 10 000 Da to 150 000 Da. Dextran-T10 has a molecular weight of 10 000 Da. Bovine serum albumin (BSA) is a protein with a molecular weight around 69 000 Da. The diffusivity and the osmotic pressure of BSA solutions are affected by the pH and ionic strength, so care was taken choosing, in the literature, correlations of the physical properties for pre-defined values of pH and ionic strength. The diffusivity of a protein in solution depends on the interactions between the molecules. These interactions change with the concentration of the protein and also with the associated charge. The charge is a function of the pH of the solution and has a minimum value at the isoelectric point. At the isoelectric point, the BSA-BSA and BSA-membrane interactions are minimized and so is the diffusivity of the protein. Since the physical properties used were those for pre-defined values of pH and ionic strength, BSA-BSA interactions are already reflected in the physical properties. However, BSA-membrane interactions are not taken into account by the model, but since the cell operates at the isoelectric point of BSA, these interactions are small. The diffusivity of Dextrans of low molecular weights (Dextran-T10) is constant for diluted solutions until concentrations around 100 kg/m³ (Laurent et al. [32]), and for this reason a constant value (10.5×10^{-11} m²/s) taken from Bhattacharya et al. [33] was used in this study.

The viscosity of the mixture ($\bar{\mu}$) was obtained by:

$$\bar{\mu} = \mu_{BSA} x_{BSA} + \mu_{DT10} x_{DT10} \quad (5.7)$$

where μ_{BSA} is the viscosity of a BSA solution, μ_{DT10} is the viscosity of a Dextran-T10 solution, and x_{BSA} and x_{DT10} are the mass fractions of BSA and Dextran-T10, respectively.

The osmotic pressure of each component, BSA and Dextran-T10, is non-linearly dependent on the respective concentration:

$$\pi_i = k_1^i C_i + k_2^i C_i^2 + k_3^i C_i^3 \quad (5.8)$$

The values k_1^i , k_2^i and k_3^i were obtained from Jonsson [34] (Dextran-T10) and from Leung and Probstein [35] (BSA).

The viscosity, the diffusivity, and the osmotic pressure of each solute, for a solution with pH 4.7 and an ionic force of 0.15 M, are listed in Table 5.2.

Table 5.2 – Viscosity, diffusivity and osmotic pressure of BSA and Dextran-T10.

<i>Equations</i>		
<i>Property</i>	BSA	Dextran-T10
Viscosity (Pa.s)	$\mu_{BSA} = 9.086 \times 10^{-4} \exp(2.44 \times 10^{-5} C^2)$ Gill et al. [36]	$\mu_{DT10} = 10^{-3} + 1.85 \times 10^{-5} C - 5.0 \times 10^{-8} C^2 + 6.67 \times 10^{-10} C^3$ Field and Aimar [37]
Diffusivity (m ² /s)	$D_{BSA} = (7 - 0.0041C) \times 10^{-11}$ Leung and Probstein [35]	$D_{DT10} = 10.5 \times 10^{-11}$ S. De and P. K. Bhattacharya [33]
Osmotic pressure (Pa)	$\pi_{BSA} = 2.3 \times 10^2 C - 1.34 C^2 + 3.09 \times 10^{-3} C^3$ Leung and Probstein [35]	$\pi_{DT10} = 1.116 \times 10^3 C - 4.91 C^2 + 2.57 \times 10^{-2} C^3$ Jonsson [34]

5.3.3. Transmission model

The transmission of the solutes across the membrane was described by a convective-diffusive transport model (Opong and Zydney [29, 38]). The rejection coefficient of component i is given by:

$$R_i = 1 - \frac{S_{i,\infty} \exp\left[\left(S_{i,\infty} V_m \delta_m\right) / D_{i,\text{eff}}\right]}{S_{i,\infty} + \exp\left[\left(S_{i,\infty} V_m \delta_m\right) / D_{i,\text{eff}}\right] - 1} \quad (5.9)$$

where $S_{i,\infty}$ is the asymptotic intrinsic sieving coefficient of the component i , δ_m the membrane thickness and $D_{i,\text{eff}}$ the effective diffusivity of the component i along the membrane pore. The effective diffusivity is given by:

$$D_{i,\text{eff}} = D_i \phi_{p,i} K_i^d \quad (5.10)$$

where $\phi_{p,i}$ is a constant of proportionality representing the equilibrium partition coefficient and K_i^d is the diffusive hindrance factor. The constant of proportionality $\phi_{p,i}$, according to Opong and Zydney [29], is given by:

$$\phi_{p,i} = (1 - \lambda_i)^2, \quad 0 < \lambda_i < 1 \quad (5.11)$$

where the parameter λ_i depends on the equivalent molecular radius of the component i , r_i^* , and on the specific area of the pores of the membrane, s :

$$\lambda_i = \frac{r_i^*}{2s} \quad (5.12)$$

The equivalent molecular radius of the molecules of BSA and Dextran-T10 and the values of the parameter λ_i for the OMEGA Polysulfone Membrane 50 kDa MWCO are listed in Table 5.3. The equivalent molecular radius of BSA was determined based on data from Tencer et al. [39], and the equivalent molecular radius of Dextran-T10 was taken from Granath and Kvist [40]. The specific area of the pores of the membrane was determined based on the experimental data of Opong and Zydney [29].

Table 5.3 - Values of λ_i and r_i^* .

Component	r_i^* (nm)	λ_i^*
BSA	3.04	0.830
DextranT10	2.33	0.645

* Relative to OMEGA Polysulfone Membrane (50 kDa MWCO)

According to Opong and Zydney [29] the asymptotic intrinsic sieving coefficient of the component i , $S_{i,\infty}$, is proportional to the convective hindrance factor, K_i^c :

$$S_{i,\infty} = \phi_{p,i} K_i^c \quad (5.13)$$

where $\phi_{p,i}$ is the constant of proportionality.

The convective and diffusive hindrance factors, K_i^c and K_i^d , which are dependent on the values of λ_i , were determined considering axisymmetric pores and spherical particles by the procedure described by Opong and Zydney [29].

5.3.4. Domain and numerical grid

Previous work has shown [23, 24] that there are two critical factors for the selection of a grid to simulate Hybrid Membrane Cells:

- a) the number of nodes in the normal direction must be sufficiently high to resolve the non-linear concentration profiles typical of high surface concentrations;
- b) the number of nodes along the tangential direction must be sufficiently high to resolve the abrupt concentration change in the boundary between semi-permeable and fully-permeable membranes sub-sections.

Since high-density grids are necessary to accurately represent the concentration variation at the beginning of each fully-permeable sub-section, the number of grid nodes needed to solve accurately the flow and mass transport equations increases with the number of membrane sections. As the number of nodes of the grid increases, the computational resources required become too high. This is why the equations for cells with four or fewer membrane sections were solved in a single grid, while cells with more than four membrane sections were solved by decomposing the domain in several grids, one for each section (more details are in Miranda and Campos [23]).

To determine the number of nodes necessary in the normal direction, grid tests were made for a conventional membrane and for the highest feed concentrations and transmembrane pressures studied, i.e., high solute concentrations at the membrane surface. The independent parameter chosen to perform these tests was the discretization error expressed by:

$$\mathcal{E}_{\bar{c}_i^m} = \frac{\bar{c}_i^{m,ref} - \bar{c}_i^m}{\bar{c}_i^{m,ref}} \quad (5.14)$$

where $\bar{c}_i^m$ refers to the normalized concentration of component i at the membrane surface. The results are summarized in Table 5.4.

Table 5.4 – Grid tests for the normal direction ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\Delta P = 2.28 \times 10^5 \text{ Pa}$, $n = 1$ and $l_m = 500$).

Grid ($n \times m$)	ni_m^*	$\mathcal{E}_{\bar{c}_{BSA}^m}$	$\mathcal{E}_{\bar{c}_{DT10}^m}$
225×126	208	3.01%	2.85%
225×251	208	1.21%	1.16%
225×501	208	ref. grid	ref. grid

* ni_m is the number of grid nodes along the membrane section

To determine the number of nodes necessary in the tangential direction, grid tests were made for a Hybrid Membrane Cell with 4 sections, for the highest fully-permeable velocity, highest feed concentration, and highest transmembrane pressure.

Table 5.5 – Grid tests for the tangential direction ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $v_m^f = 5 \times 10^{-5}$, $\Delta P = 2.28 \times 10^5 \text{ Pa}$, $n = 4$ and $l_m = 555$).

Grid ($n \times m$)	ni_m^*	$\mathcal{E}_{\bar{c}_{BSA}^-}$	$\mathcal{E}_{\bar{c}_{DT10}^-}$
257×251	241	2.25 %	0.86 %
497×251	481	0.67 %	0.26 %
977×251	961	ref. grid	ref. grid

* ni_m is the number of grid nodes along the membrane section

The results (Table 5.5) show that a grid of 497×251 is sufficient to obtain an error of less than 1%. This grid was used for all simulations in Hybrid Membrane Cells with 4 sections. Hybrid Membrane Cells with more than 4 sections were simulated with several grids of similar density.

5.3.5. Boundary conditions

At the cell inlet and outlet, the flow is fully developed. The momentum and mass fluxes are null through the middle plane of the cell. Conditions for boundaries I, II, III, VI and VII (Figure 5.2) have been presented by Afonso et al. [30] and Miranda and Campos [23, 31, 41] and are listed in Table 5.6.

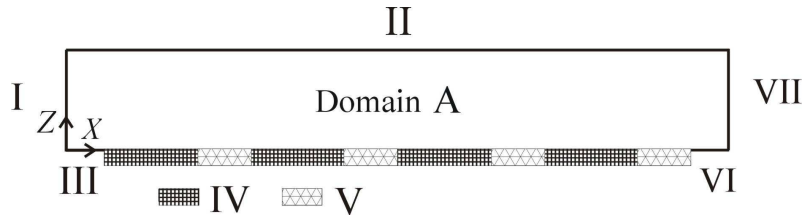


Figure 5.2 - Schematic representation of the domain of a cell with four membrane sections and respective boundaries.

Table 5.6 - Conditions for boundaries I, II, III, VI and VII.

I	II	III	VI	VII
$v_x = \frac{3}{2} [1 - 4(0.5 - z)^2]$	$\frac{\partial v_x}{\partial z} = 0$	$v_x = 0$	$v_x = 0$	$\frac{\partial v_x}{\partial x} = 0$
$v_z = 0$	$v_z = 0$	$v_z = 0$	$v_z = 0$	$\frac{\partial v_z}{\partial x} = 0$
$\psi = \frac{3(0.5 - z)}{2} - \frac{(0.5 - z)^3}{2}$	$\psi = 0$	$\psi = \frac{11}{16}$	$\psi = \frac{11}{16} + \int -v_z \, dx$	$\frac{\partial \psi}{\partial x} = 0$
$\omega = 12(0.5 - z)$	$\omega = 0$	$\omega = \frac{\partial v_x}{\partial z}$	$\omega = \frac{\partial v_x}{\partial z}$	$\frac{\partial \omega}{\partial x} = 0$
$c_i = 1$	$\frac{\partial c_i}{\partial z} = 0$	$\frac{\partial c_i}{\partial z} = 0$	$\frac{\partial c_i}{\partial z} = 0$	$\frac{\partial c_i}{\partial x} = 0$
$\phi_i = 0$	$\frac{\partial \phi_i}{\partial z} = 0$	$\frac{\partial \phi_i}{\partial z} = 0$	$\frac{\partial \phi_i}{\partial z} = 0$	$\frac{\partial \phi_i}{\partial x} = 0$

Boundary conditions for the semi-permeable membranes (boundaries IV) were analyzed by Miranda and Campos [31, 41], but, in the present study, they must be modified to take into account the transmission through the membrane. They are going to be briefly discussed in conjunction with the boundary conditions for the fully-permeable membranes (boundaries V).

The slip velocity at the interface between a flowing fluid and a porous material can be neglected for all membrane pressure driven processes (Belfort and Nagata [42]). Then, as long as membranes with pore sizes and porosities much larger than those used in microfiltration processes are not used as fully-permeable membranes, the no-slip condition can be adopted for all membranes in the cell.

The permeate velocity, normal component, at the semi-permeable membranes, can be expressed [43] by the ratio between the driving force and the resistance to the flow:

$$-v_z = \frac{\Delta P - (\Delta\pi_{BSA} + \Delta\pi_{DT10})}{\bar{\mu}_p^s R_m^s V_0} = \frac{\Delta P - (\pi_{BSA}^m - \pi_{BSA}^p) - (\pi_{DT10}^m - \pi_{DT10}^p)}{\bar{\mu}_p^s R_m^s V_0} \quad \text{at } z = 0 \quad (5.15)$$

where π_i^m and π_i^p represent the osmotic pressure at the membrane surface and in the permeate flux respectively, R_m^s the resistance of the semi-permeable membrane and $\bar{\mu}_p^s$ the viscosity of the permeate flux that crosses the semi-permeable membrane.

The osmotic pressure is a function of the concentration of the solutes. This dependence can be expressed in terms of the rejection coefficients.

For the fully-permeable sub-sections, the osmotic pressure difference across the membrane is zero and the permeate velocity is then given by:

$$v_m^f = \frac{\Delta P^f}{\bar{\mu}_p^f R_m^f V_0} \quad (5.16)$$

where the superscript f indicates that the variables are for a fully-permeable sub-section.

At the surface of the semi-permeable membranes, $z = 0$, and for each component, the difference between the normal convective flux promoted by suction and the flux through the

membrane is equal to the diffusive flux in the opposite direction promoted by the concentration gradient between the membrane surface and the bulk:

$$-\frac{1}{Pe_i} \frac{\partial c_i}{\partial z} = v_m^s (c_i^m - c_i^p) \quad (5.17)$$

For the fully-permeable membrane, $c_i^m = c_i^p$, so

$$\frac{1}{Pe_i} \frac{\partial c_i}{\partial z} = 0 \quad (5.18)$$

Equation 5.18 presupposes that the pore size of the fully-permeable membrane is large compared with the size of the molecules of the solutes.

5.3.6. Convergence of the numerical method

The convergence of the numerical method was checked calculating the total residues of the discretized equations (R_t) and analysing the evolution of the relative difference, in two consecutive iterations, of the values of the concentration (ε_{crit}), for both components, in a critical point of the cell located near the end of the membrane section ($x - l_{in} = 539$).

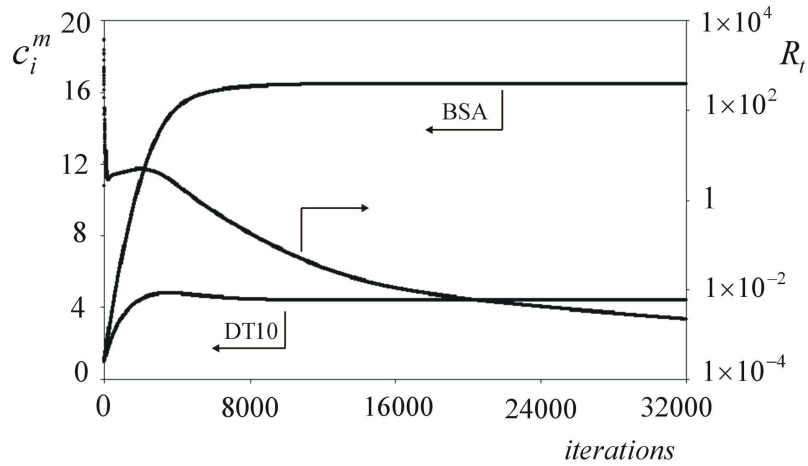


Figure 5.3 – Total residues of the vorticity and mass transport equations and concentrations of BSA and Dextran-T10 at a critical node ($x - l_{in} = 539$) as a function of the number of iterations ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $v_m^f = 5 \times 10^{-5} \text{ m/s}$, $\Delta P = 2.28 \times 10^5 \text{ Pa}$, $\varepsilon = 0.1$, $n = 4$ and $l_m = 555$).

The evolution of these parameters is represented in Figure 5.3 for severe, in terms of convergence, operation conditions. The data of Figure 5.3 show that concentration converges to a constant value and, at the same time, the residuals decrease to a small value, $R < 10^{-2}$. Based on this result, the following convergence criteria were adopted:

$$\begin{cases} \varepsilon_{crit} < 10^{-3} \\ R_t < 10^{-2} \end{cases} \quad (5.19)$$

5.4. Results and discussion

5.4.1. Concentration at the membrane surface

The concentrations of the components at the membrane surface are represented in Figure 5.4. These concentration profiles were obtained under conditions of high polarization. In the conventional cell, the concentration of the components increases monotonically along the membrane surface, while in the Hybrid Membrane Cell the concentration of the components increases along the semi-permeable sub-sections and decreases along the fully-permeable sub-sections. The cleaning effect and the re-built of a new mass boundary are clearly observed in the Figure 5.4. The maximum concentration is therefore higher in the conventional cell: the normalized BSA concentration reaches the value of 9.1 in the conventional cell, while in the Hybrid Membrane Cell the maximum is 7.6.

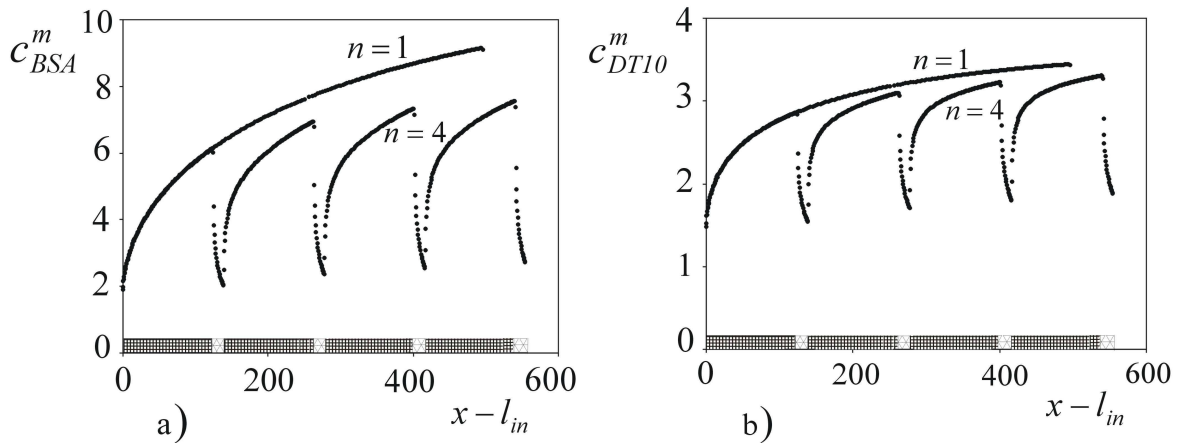


Figure 5.4 – Concentrations along the membrane surface for a conventional membrane cell and for a Hybrid Membrane Cell ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\Delta P = 1.14 \times 10^5 \text{ Pa}$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$): a) BSA, b) Dextran-T10.

Experimental results using conventional cells have shown that protein transmission increases with polarization [6-8, 12-14]. The numerical results confirm this functionality and they go further:

- a) both, the polarization and the concentrations of BSA and Dextran-T10 in the permeate side increase along x ;
- b) the cleaning effect of the Hybrid Membranes Cell leads to a simultaneous reduction of the polarization and of the concentration of the solutes in the permeate side (Figure 5.5).

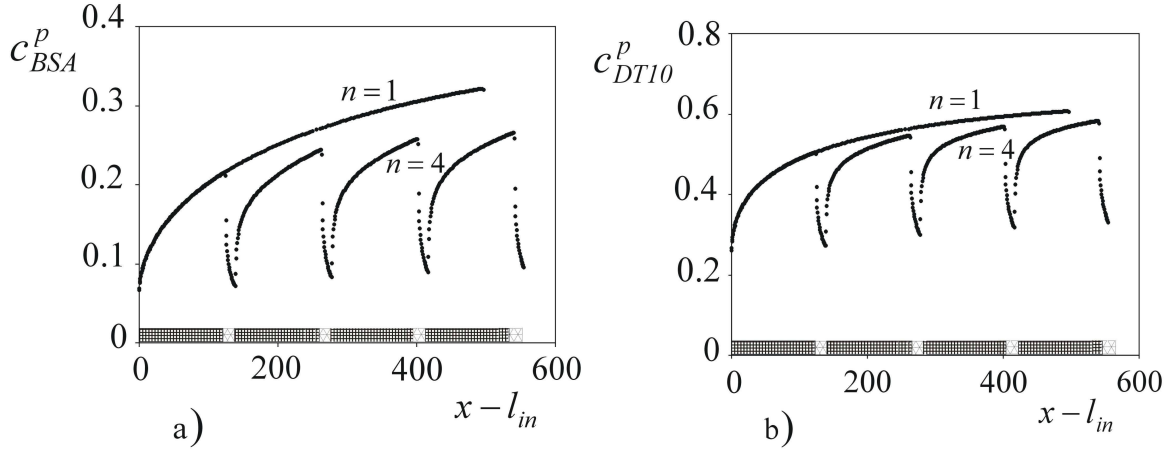


Figure 5.5 – Permeate concentrations along the membrane for a conventional membrane cell and for a Hybrid Membrane Cell ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$,

$$V_0 = 1.632 \text{ m/s}, Pe_{BSA}^0 = 2.36 \times 10^7, Pe_{DT10}^0 = 1.55 \times 10^7, \Delta P = 1.14 \times 10^5 \text{ Pa},$$

$$\varepsilon = 0.1 \text{ and } v_m^f = 1 \times 10^{-5}) : \text{a) BSA, b) Dextran-T10.}$$

5.4.2. Selectivity

The apparent selectivity continuously decreases along a conventional cell (Figure 5.6) because BSA concentrations at the membrane surface and in the permeate increase more than the concentrations of Dextran-T10. The higher accumulation of BSA leads to a higher transmission and consequently to a reduction of the selectivity. In a Hybrid Membrane Cell, the selectivity increases after each fully-permeable sub-section because the polarized layer is cleaned and the transmission of BSA decreases much more than the transmission of Dextran-T10. This result is consistent with experimental results in conventional cells [12-14], which show a decrease of selectivity associated with the simultaneous increase of polarization.

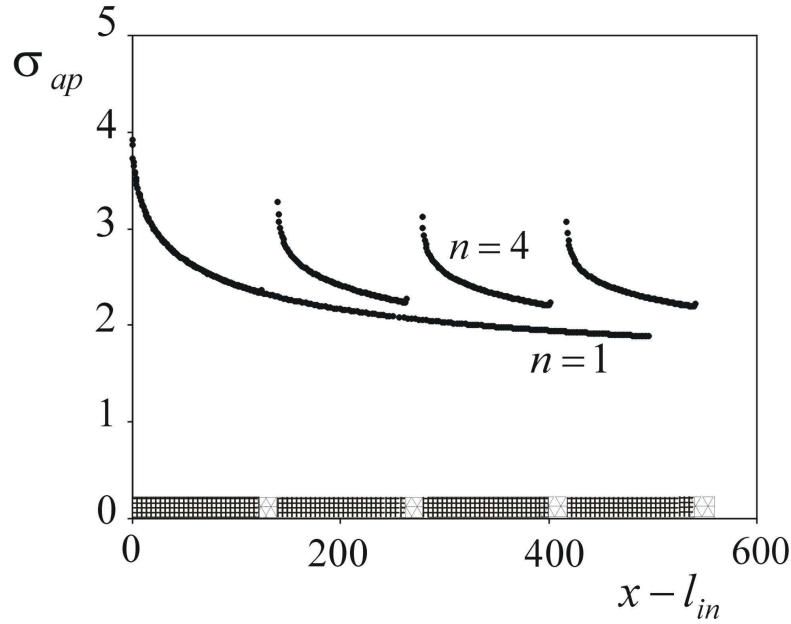


Figure 5.6 – Local apparent selectivity along the membrane for a conventional membrane cell and for a Hybrid Membrane Cell ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\Delta P = 1.14 \times 10^5 \text{ Pa}$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$).

The local selectivity was used to determine the mean selectivity of the cell as function of the transmembrane pressure (Figure 5.7). In a conventional cell, the selectivity increases with the transmembrane pressure until it reaches a maximum for $\Delta P = 3.80 \times 10^4 \text{ Pa}$. For transmembrane pressures above $3.80 \times 10^4 \text{ Pa}$, the selectivity decreases due to the polarization of the membrane. According to Figure 5.7, in the region of high polarization, the mean selectivity of a Hybrid Membrane Cell is higher than the mean selectivity of the conventional cell.

The suitability of Hybrid Membrane Cells to promote the fractionation of two solutes was measured by comparing the ratio between the apparent selectivity of the separation in a Hybrid Membrane Cell and the apparent selectivity in a conventional cell. This ratio was studied as a function of the transmembrane pressure and for two values of the inlet concentration of the solutes ($C_{BSA}^0 = C_{DT10}^0 = 0.05 \text{ kg m}^{-3}$ and $C_{BSA}^0 = C_{DT10}^0 = 24.4 \text{ kg m}^{-3}$) and three values of the velocity over the fully-permeable membrane (Figure 5.8).

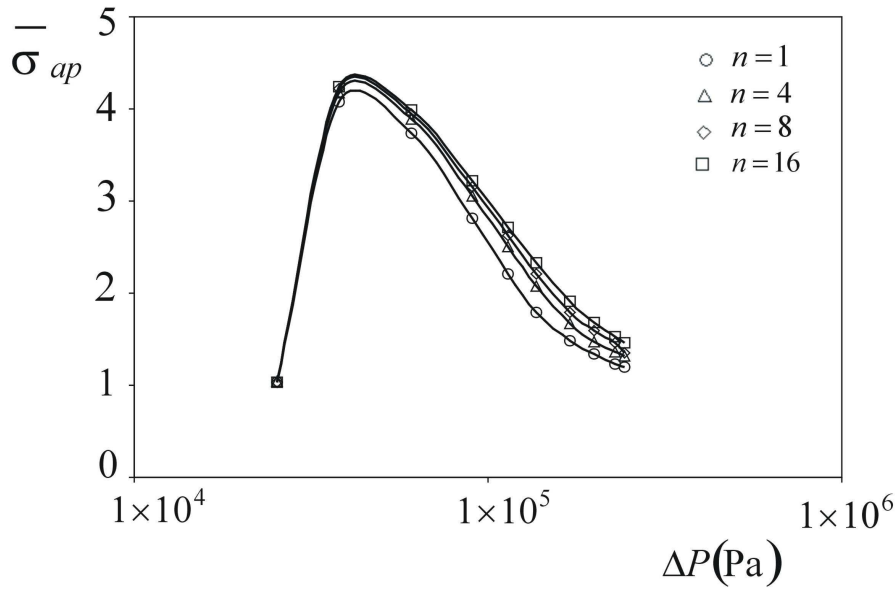


Figure 5.7 – Mean apparent selectivity versus transmembrane pressure ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$).

The selectivity ratio is significantly higher than 1 for a large range of values of the transmembrane pressure in which the membrane is polarized. The ratio is dependent on the feed concentration: for low feed concentrations the ratio is higher. However, for low feed concentrations and high transmembrane pressures the effect of hybrid membranes is negligible.

The selectivity ratio is also dependent on the flow rate across the fully-permeable membrane. The flow rate across the fully-permeable membrane may increase by increasing the permeate velocity over the fully-permeable membrane or the fraction of the fully-permeable membrane area, ε . According to Figure 5.8, for a feed concentration of 24.4 kg m^{-3} , the maximum ratio for $v_m^f = 1 \times 10^{-6}$ is 1.03 and for $v_m^f = 5 \times 10^{-5}$ is 1.3. According to Figure 5.9, this ratio increases with ε .

In Figure 5.9 the curve for $\varepsilon = 0.357$ and $v_m^f = 1 \times 10^{-5}$ has the same flow rate as the curve for $\varepsilon = 0.1$ and $v_m^f = 5 \times 10^{-5}$. The selectivity ratios for both curves are almost identical, an indication that the primary variable which determines the selectivity is not the fraction of the

fully-permeable membrane area or the velocity across the fully-permeable membrane but the flow rate.

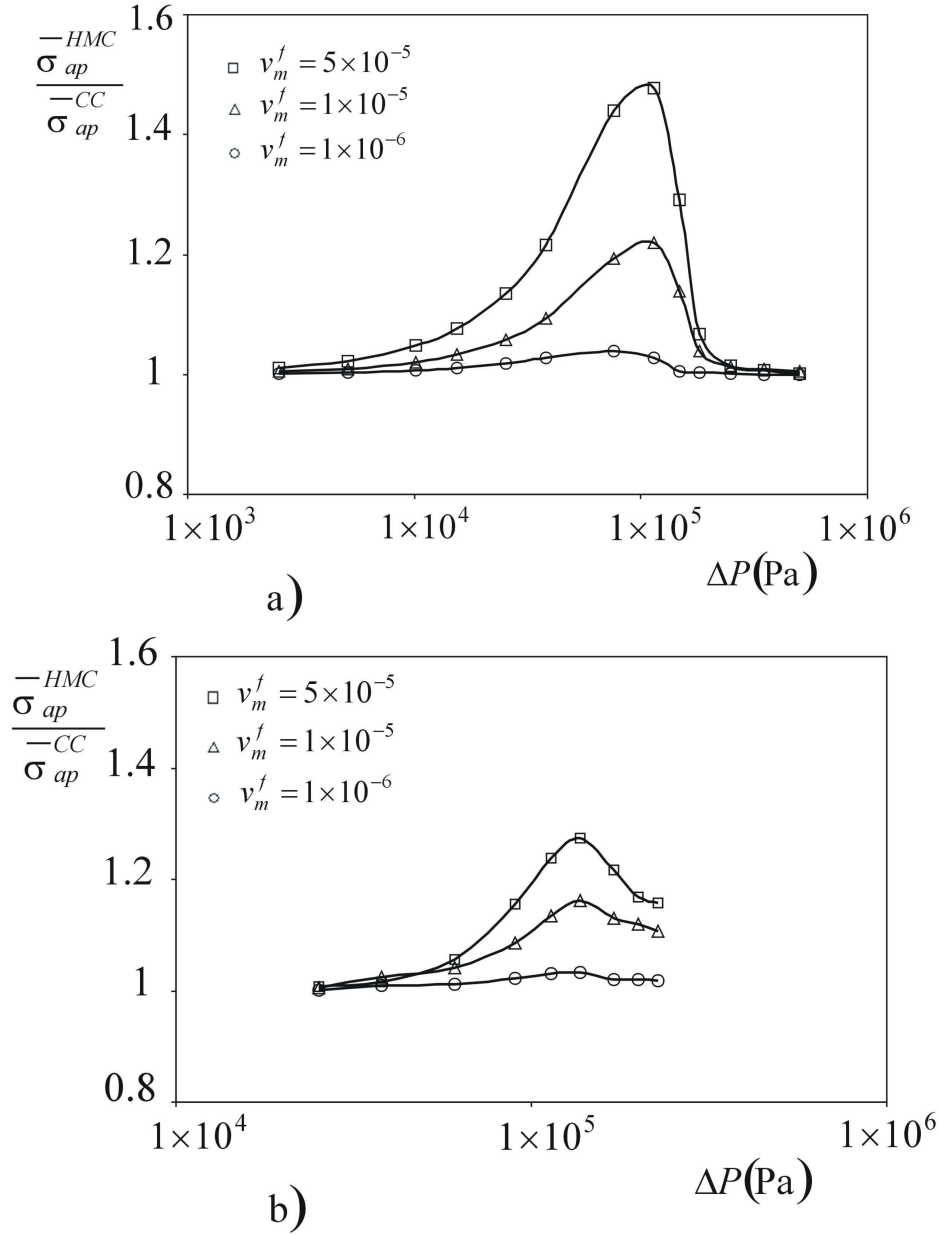


Figure 5.8 – Ratio between apparent selectivity in a Hybrid Membrane Cell ($\varepsilon = 0.1$, $n = 4$) and apparent selectivity in a conventional cell as a function of transmembrane pressure for three values of the velocity across the fully-permeable membrane ($v_m^f = 5 \times 10^{-5}$, $v_m^f = 1 \times 10^{-5}$ and $v_m^f = 1 \times 10^{-6}$): a) $C_{BSA}^0 = 0.05 \text{ kg/m}^3$, $C_{DT10}^0 = 0.05 \text{ kg/m}^3$, $Re_0 = 1387$ ($V_0 = 1.324 \text{ m/s}$), $Pe_{BSA}^0 = 1.89 \times 10^7$ and $Pe_{DT10}^0 = 1.26 \times 10^7$; b) $C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$ ($V_0 = 1.632 \text{ m/s}$), $Pe_{BSA}^0 = 2.36 \times 10^7$ and $Pe_{DT10}^0 = 1.55 \times 10^7$.

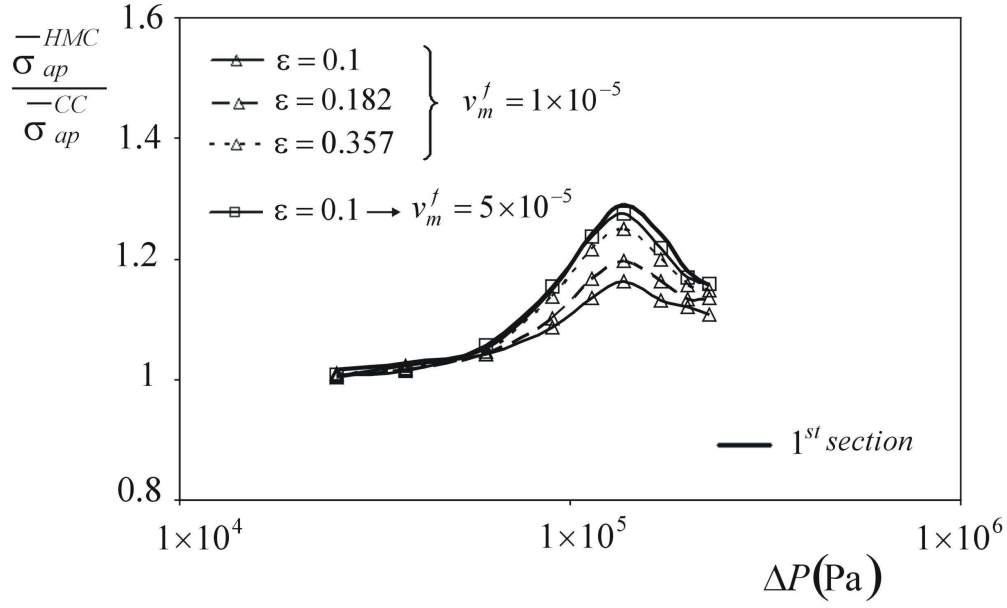


Figure 5.9 – Ratio between apparent selectivity in a Hybrid Membrane Cell ($n = 4$) and the apparent selectivity in a conventional cell as a function of transmembrane pressure for the first section and for three values of ε ($\varepsilon = 0.1$, $\varepsilon = 0.182$ and $\varepsilon = 0.357$); $C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $\text{Re}_0 = 1387$ ($V_0 = 1.632 \text{ m/s}$), $\text{Pe}_{BSA}^0 = 2.36 \times 10^7$ and $\text{Pe}_{DT10}^0 = 1.55 \times 10^7$.

There is an upper limit above which increasing flow rates cease to significantly improve the selectivity of the hybrid cell. For sufficiently high flow rates, the boundary layer is completely cleaned (see Miranda and Campos [23] for details). In this case, the selectivity as a function of x is a periodic function with the same pattern repeating itself along the membrane. Figure 5.10 shows the selectivity along the membrane for a low flow rate and for a high flow rate. For the low flow rate, the selectivity decreases from one section to the next. For a high flow rate the selectivity remains constant from section to section. The maximum selectivity possible is therefore the mean selectivity of the first section. The curve for the maximum selectivity, represented in Figure 5.9, is slightly above the curve for $\varepsilon = 0.1$ and $v_m^f = 5 \times 10^{-5}$, so the flow rate, for this condition, is sufficient to obtain a selectivity near the maximum possible.

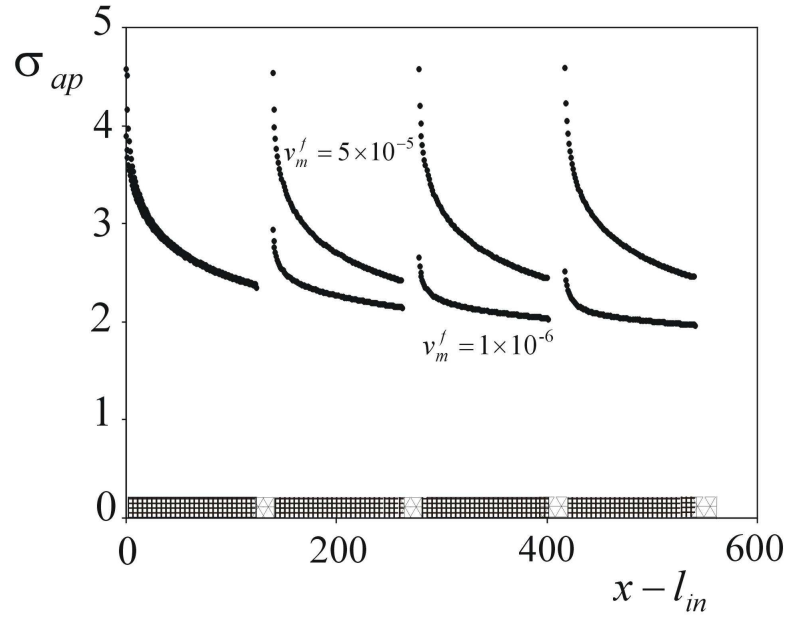


Figure 5.10 – Apparent selectivity along the membrane in a Hybrid Membrane Cell ($n = 4$) for two values of permeate velocity at fully-permeable membranes ($v_m^f = 5 \times 10^{-5}$ and $v_m^f = 1 \times 10^{-6}$);

$$\varepsilon = 0.1, C_{BSA}^0 = 24.4 \text{ kg/m}^3, C_{DT10}^0 = 24.4 \text{ kg/m}^3, \text{Re}_0 = 1387 \text{ } (V_0 = 1.632 \text{ m/s}),$$

$$\text{Pe}_{BSA}^0 = 2.36 \times 10^7 \text{ and } \text{Pe}_{DT10}^0 = 1.55 \times 10^7, \Delta P = 1.14 \times 10^5 \text{ Pa.}$$

5.4.3. Number of sections

The apparent selectivity can be further increased by increasing the number of sections of the Hybrid Membrane Cell. Figure 5.11 shows the selectivity ratio obtained for $C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$ and $v_m^f = 1 \times 10^{-5} \text{ m/s}$. The results show that selectivity increases with the number of sections. This result is expected since, as the number of sections increases, the semi-permeable sections are shorter and the boundary layer is cleaned in more locations along the membrane.

Figures 5.7 and 5.11 show that the performance of a hybrid membrane cell can improve by increasing the number of sections (keeping the cell length constant). The implementation of a hybrid membrane cell with a high number of sections requires micrometric precision techniques to manufacture very short membranes with different permeabilities and a support with independent collectors. Hybrid membranes with transversal patches with micrometric precision can be produced by combining the phase inversion technique with ink jet printing [44-46] using an ink jet dispenser.

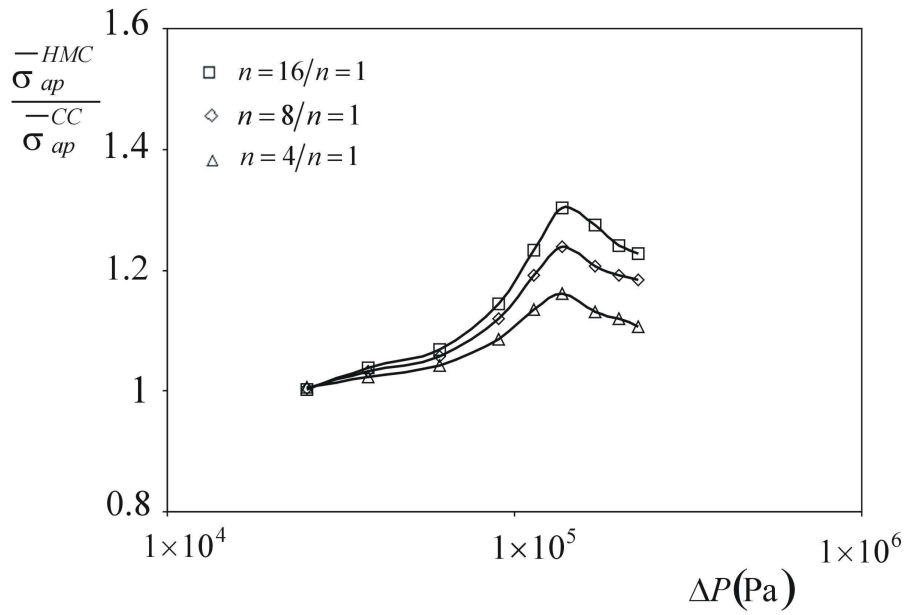


Figure 5.11 - Ratio between apparent selectivity in a Hybrid Membrane Cell and in a conventional cell as a function of transmembrane pressure ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$).

5.4.4. Concentration dependent properties

In ultrafiltration, when polarization increases, the variation of the transport properties (viscosity and diffusivity) with the concentration becomes important. The diffusivity decreases and the viscosity increases significantly with concentration. The variation of transport properties with polarization leads to a reinforcement of the polarization, and consequently it contributes to a low selectivity. Hybrid Membrane Cells have a beneficial effect on the variation of physical properties, since the concentration is reduced, the local Reynolds number increases and the local Peclet number decreases. The cleaning of the boundary layer interrupts the increase of the Peclet and Reynolds numbers in the vicinity of the membrane (Figures 5.12 and 5.13) and the transport properties do not reach extreme values.

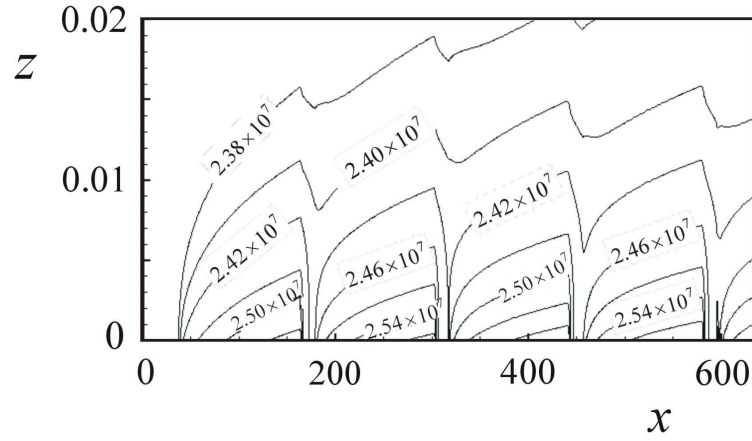


Figure 5.12 – Peclet number of BSA in a region near the membrane ($z < 0.02$), $C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $v_m^f = 1 \times 10^{-5}$, $\Delta P = 1.14 \times 10^5 \text{ Pa}$, $\varepsilon = 0.1$ and $n = 4$.

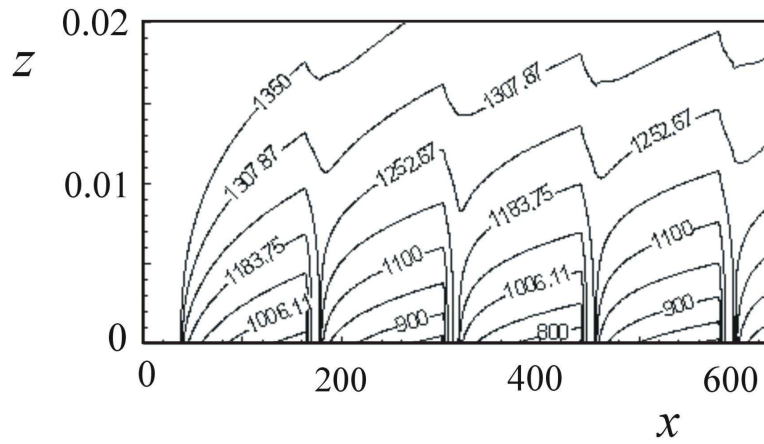


Figure 5.13 - Reynolds number in a region near the membrane ($z < 0.02$), $C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $v_m^f = 1 \times 10^{-5}$, $\Delta P = 1.14 \times 10^5 \text{ Pa}$, $\varepsilon = 0.1$ and $n = 4$.

5.4.5. Recovery of BSA in the BSA – rich stream

One of the advantages of the Hybrid Membrane Cell is that it enables the recovery, in the stream that crosses the fully-permeable membranes, of the component rejected by the semi-permeable sub-sections. This is so because the flow that crosses the fully-permeable membrane comes from the boundary layer over the semi-permeable membrane.

Figure 5.14 shows the selectivity of this secondary separation as a function of the transmembrane pressure. The selectivity of the fully-permeable membranes increases with transmembrane pressure. This is due to the increase of the polarization of BSA; it increases much more than the polarization of Dextran-T10 along the semi-permeable membrane.

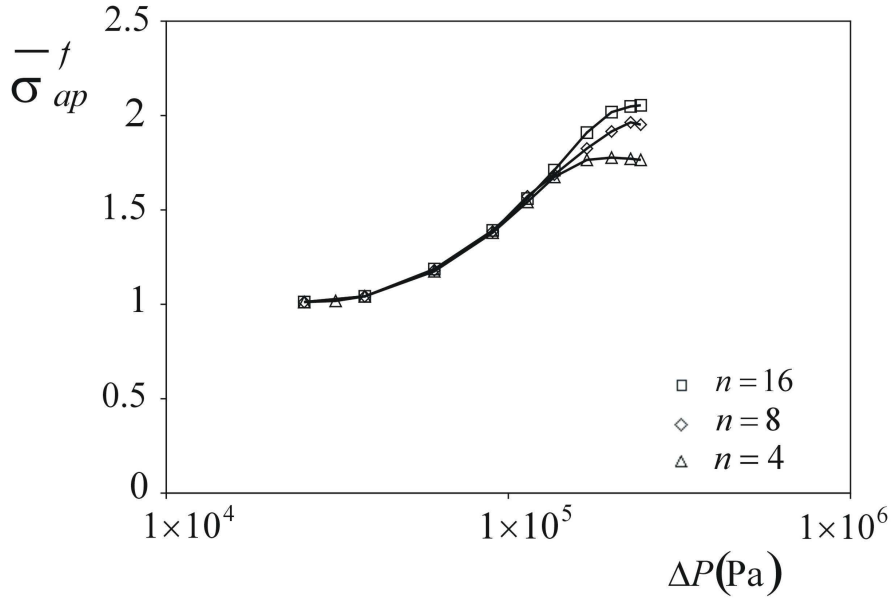


Figure 5.14 - Mean apparent selectivity of fully permeable sub-sections versus transmembrane pressure ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$).

In the study by Pinto et al. [24], a Hybrid Membrane Cell was combined with a differential diffusion mechanism to separate two solutes. The semi-permeable membranes were permeable to the solvent but impermeable to both solutes and the fully-permeable membranes were permeable to all the components of the solution. With this type of arrangement, the stream crossing the fully-permeable membranes was rich in the less diffusive solute (BSA). This less diffusive solute is also the most rejected by the semi-permeable membranes of the present study.

Figure 5.15 compares the selectivity in the fully-permeable stream of the cell studied by Pinto et al. [24] with the selectivity in the fully-permeable stream of the cell studied in the present work. The data show that the selectivity in the fully-permeable stream is lower when the semi-permeable membranes are not selective (Pinto et al. [24]). This lower selectivity is

justified by the higher concentration of Dextran-T10 (total rejection) over the semi-permeable membranes.

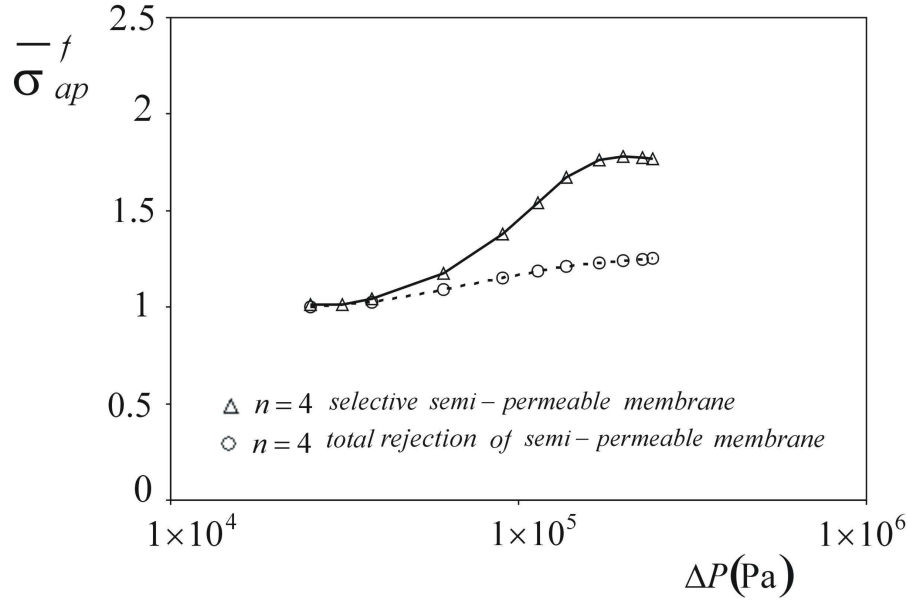


Figure 5.15 - Mean apparent selectivity of fully permeable sub-sections versus transmembrane pressure ($n = 4$, $C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$). Comparison between a cell with selective semi-permeable membranes (present work) and a cell with semi-permeable membranes that completely reject both solutes (Pinto et al. [24]).

5.4.6. Permeate velocity

Since the boundary layer is interrupted by the fully-permeable membrane sub-sections, polarization is reduced in the Hybrid Membrane Cell. For this reason the mean permeate velocity across the semi-permeable membranes of a Hybrid Membrane Cell is higher than the mean permeate velocity in a conventional cell for the same operating conditions. Figure 5.16 shows the ratio between the mean permeate velocity across the semi-permeable membranes of a Hybrid Membrane Cell and the mean permeate velocity in a conventional cell. The ratio increases for transmembrane pressures for which the membrane is polarized ($\Delta P > 1.14 \times 10^5 \text{ Pa}$).

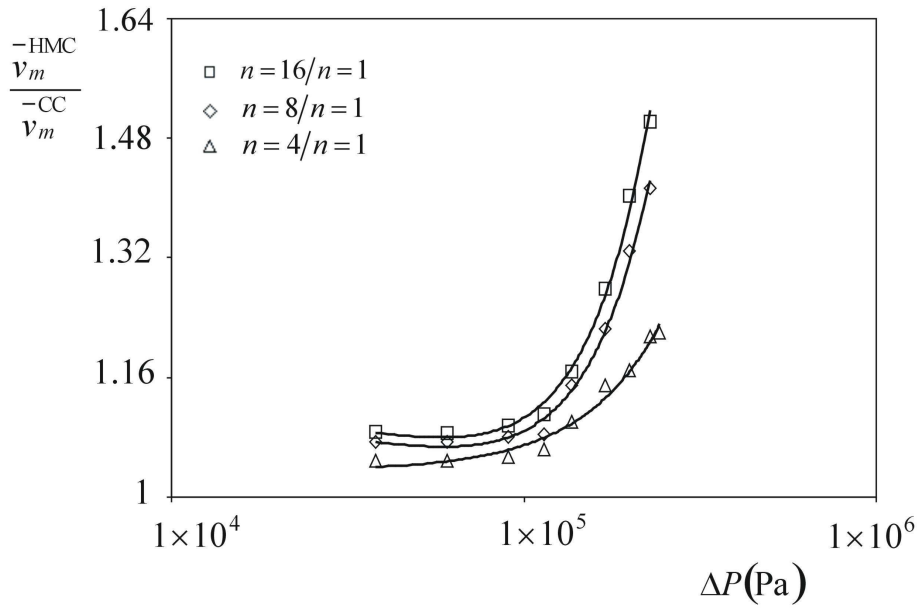


Figure 5.16 - Ratio between mean velocity over semi-permeable membranes of a Hybrid Membrane Cell and permeate velocity of a conventional cell as a function of the transmembrane pressure ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$).

5.4.7. Operational flexibility

In summary, the results show that a Hybrid Membrane Cell has a higher operational flexibility than a conventional cell. The selectivity of a conventional membrane reaches a maximum for low values of the transmembrane pressure, and afterwards, it decreases significantly. However, a high transmembrane pressure is required to reach a high permeate velocity and, consequently, a high productivity. Therefore, in conventional cells, a trade-off must exist between selectivity and productivity, since any gain in productivity is balanced by a decrease in selectivity. In a Hybrid Membrane Cell, the loss in selectivity is smaller and is compensated by an increase of the selectivity of the fully-permeable membrane sub-sections and by an increase of the permeate velocity.

As shown in Figure 5.17, the advantages of hybrid membranes are higher for high transmembrane pressures.

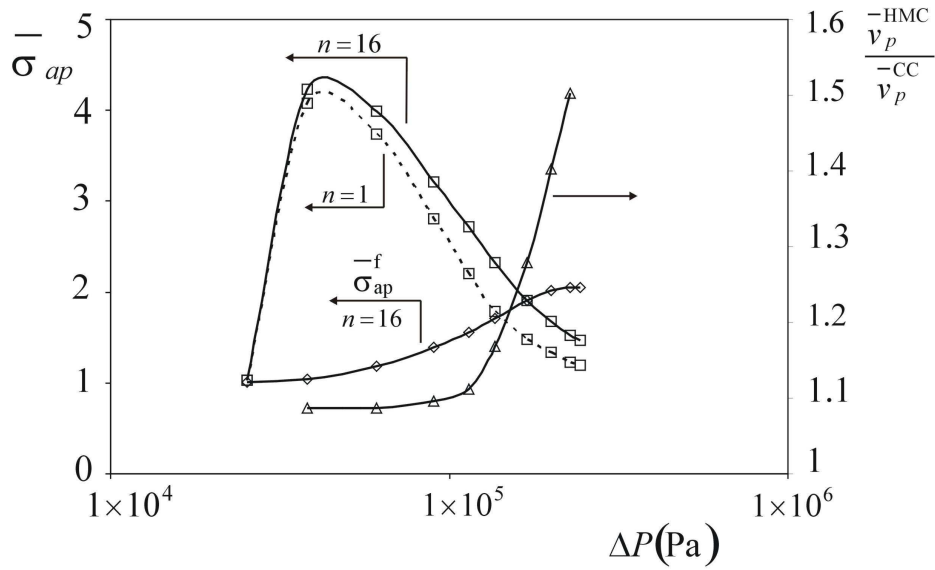


Figure 5.17 - Mean apparent selectivity of a Hybrid Membrane Cell ($n=16$) and in a conventional cell ($n=1$), mean apparent selectivity of fully-permeable sub-sections ($n=16$) and ratio of the mean permeate velocity between Hybrid Membrane Cell and a conventional cell, all as a function of transmembrane pressure ($C_{BSA}^0 = 24.4 \text{ kg/m}^3$, $C_{DT10}^0 = 24.4 \text{ kg/m}^3$, $Re_0 = 1387$, $V_0 = 1.632 \text{ m/s}$, $Pe_{BSA}^0 = 2.36 \times 10^7$, $Pe_{DT10}^0 = 1.55 \times 10^7$, $\varepsilon = 0.1$ and $v_m^f = 1 \times 10^{-5}$).

5.5. Conclusions

The fractionation of an aqueous solution containing BSA and Dextran-T10 in a Hybrid Membrane Cell, comprising semi-permeable and fully-permeable membrane sections, was studied by numerical methods. The concentration and flow fields were determined by solving the Navier-Stokes and the mass transport equations. The results show that the fully-permeable membranes clean the mass boundary layer, reducing the polarization and the transmission of the macromolecules and increasing the selectivity of the semi-permeable membranes.

The ratio between the mean selectivity of a Hybrid Membrane Cell and the selectivity of a conventional membrane was determined. In the range of transmembrane pressures for which the conventional membranes usually polarize, the selectivity ratio is significantly higher than 1, which means that the apparent selectivity in a Hybrid Membrane Cell is significantly higher than the apparent selectivity in a conventional one. The selectivity ratio

increases with the increase of flow rate across the fully-permeable membranes and with the increase of the number of sections (n). The inlet concentrations have a significant effect on the ratio for large values of the transmembrane pressure.

In a conventional cell, the diffusivity and viscosity usually increase with concentration and this phenomenon contributes to amplify the polarization. Hybrid Membrane Cells minimize the effect of concentration dependent properties because concentration is limited by the cleaning effect of the fully-permeable membranes.

Hybrid Membrane Cells brings additional flexibility to membrane fractionation processes. Hybrid Membrane Cells can operate efficiently whatever the polarization level. In conditions of high polarization, Hybrid Membrane Cells not only have a higher selectivity than conventional cells, but they have also a good selectivity in the fully-permeable membranes and a higher permeate velocity across the semi-permeable membrane sub-sections.

5.6. Nomenclature

C_i	Concentration of component i
c_i	Normalized concentration of component i
C_i^b	Concentration of component i in the bulk
C_i^0	Concentration of component i at the feed stream
C_i^m	Concentration of component i at the membrane surface
c_i^m	Normalized concentration of component i at the membrane surface
C_i^p	Concentration of component i in the stream that crosses the semi-permeable membrane
c_i^p	Normalized concentration of component i in the stream that crosses the semi-permeable membrane
$\bar{C}_i^m$	Mean concentration of component i at the membrane surface
$\bar{c}_i^m$	Mean normalized concentration of component i at the membrane surface

$\bar{c}_i^{m,ref}$	Mean normalized surface concentration of component i determined using the reference grid
D_i	Molecular diffusivity of component i
$D_{i,eff}$	Effective diffusivity of component i along the membrane pore
H	Distance between parallel plates
k_i^j	Virial coefficient of the osmotic pressure equation for component j
K_i^c	Convection hindrance factor for component i
K_i^d	Diffusive hindrance factor for component i
L_{out}	Length of the outlet section
L_{in}	Length of the inlet section
l_{in}	Normalized length of the inlet section
L_m	Total length of the membrane
l_m	Total normalized length of the membrane
L	Length of the cell
L_s	Length of a semi-permeable membrane sub-section
L_f	Length of a fully-permeable membrane sub-section
n	Number of membrane sections
ni_m	Number of grid nodes along the membrane section
R_i	Real rejection of component i
r_i^*	Equivalent molecular radius of component i
R_m^s	Resistance of the semi-permeable membrane
R_m^f	Resistance of the fully-permeable membrane
R_t	Total residual of the vorticity and mass transport equations
S_{ap_i}	Apparent sieving of a partially rejected solute
$S_{i,\infty}$	Asymptotic intrinsic sieving
s	Specific area of the pores
t	Non-dimensional time
V_0	Mean feed velocity
V_m	Permeate velocity
v_m	Normalized permeate velocity

V_m^f	Permeate velocity across the fully-permeable membrane sub-sections
v_m^f	Normalized permeate velocity across the fully-permeable membrane sub-sections
$\bar{V}_m^f$	Mean permeate velocity across the fully-permeable membrane sub-sections
$\bar{v}_m^f$	Normalized mean permeate velocity across the fully-permeable membrane sub-sections
v_m^s	Normalized permeate velocity across the semi-permeable membrane sub-sections
$\bar{v}_m^{CC}$	Normalized mean permeate velocity of a conventional cell
$\bar{v}_m^{HMC}$	Normalized permeate velocity across the semi-permeable membrane sub-sections of the Hybrid Membrane Cell
$\bar{V}_m$	Mean permeate velocity
$\bar{v}_m$	Mean normalized permeate velocity
V_x	Longitudinal component of the velocity
v_x	Normalized longitudinal component of the velocity
V_z	Vertical component of the velocity
v_z	Normalized vertical component of the velocity
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
x_i	Mass fraction of component i
Z	Vertical coordinate
z	Normalized vertical coordinate

Non-dimensional numbers

Pe_i	Peclet number of a component i
Pe_i^0	Feed Peclet number of component i
Re	Reynolds number
Re_0	Feed Reynolds number

Greek Symbols

ΔP	Static pressure difference across the semi-permeable membrane
ΔP^f	Static pressure difference across the fully-permeable membrane
π_i	Osmotic pressure of component i
$\Delta \pi_i$	Osmotic pressure difference of component i across de membrane
ε	Fraction of the area of the membrane section that is fully permeable
ε_{crit}	Numerical error of the concentration on a critical location (convergence)
$\varepsilon_{\bar{c}_i^m}$	Numerical error of the concentration (grid tests)
π^m	Osmotic pressure at the membrane surface
π^p	Osmotic pressure in the permeate
ψ	Stream function
ω	Vorticity
ρ	Density
$\bar{\mu}$	Viscosity of the mixture
$\bar{\mu}_p^s$	Viscosity of the mixture in the stream that crosses the semi-permeable membrane
$\bar{\mu}_p^f$	Viscosity of the mixture in the stream that crosses the fully-permeable membrane
μ_i	Viscosity of component i
ϕ_i	$\ln(c_i)$
σ_{ap}	Apparent selectivity
$\bar{\sigma}_{ap}$	Mean apparent selectivity
$\bar{\sigma}_{ap}^f$	Mean apparent selectivity of the fully-permeable subsections
$\bar{\sigma}_{ap}^{HMC}$	Mean apparent selectivity in a Hybrid Membrane Cell
$\bar{\sigma}_{ap}^{CC}$	Mean apparent selectivity in a conventional cell
δ_m	Membrane thickness
$\phi_{p,i}$	Equilibrium partition coefficient
λ_i	Ratio between the molecular radius of component i and 2 times the specific area of the pores

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Chapter 6

Numerical study of the effect of a charged membrane in the separation of electrically charged components

The efficiency of protein fractionation by ultrafiltration is reduced by concentration polarization, which indirectly reduces the apparent selectivity of the membrane. The complete understanding of this phenomenon requires the knowledge of the electrical interactions between the membrane and the solutes. These interactions are studied by numerical methods. A numerical code, based on a finite volume method, is developed to study the separation of a solution containing two charged solutes by solving the Poisson-Boltzmann, the Navier-Stokes and the Nernst-Planck equations. The code is used to study the effects of the electric charge of the membrane in the concentration fields of the solutes.

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6.1. Introduction

In protein fractionation by ultrafiltration, mass accumulates near the surface of the membrane, given rise to the so called concentration polarization phenomenon. Concentration polarization reduces the permeability and the selectivity of the process [1-3]. It is known that concentration polarization can be influenced by the physicochemical conditions near the membrane [4-6]. The effect of physicochemical conditions is due to ion-ion, membrane-ion, protein-ion, protein-protein [7] and membrane-protein interactions. Molecular and ionic interactions can be dealt with by modeling their effects on the diffusivity of the components and on the osmotic pressure of the solution [4,5]. However, membrane-ion and membrane-protein interactions deserved relatively less attention by researchers. Analytical and numerical methods developed so far can capture the effects of concentration dependent properties [8,9], multicomponent diffusion [10] and convection-diffusion across the membrane [11,12]. Electrical interactions between the membrane and charged components are usually neglected in most studies. However, in some separation processes, they cannot be ignored.

Here, we cover the modeling of the interactions between the membrane surface and charged components by solving numerically the electric potential equation and the flow and mass transport equations in the separation cell. Our interest is to study the separation of a solution of two species with opposite charges by a charged membrane in a parallel plate membrane cell.

6.2. Cell description

The cell under study is schematically represented in Figure 6.1. It is a parallel plate cell with a permeable membrane on both sides. The distance between the plates, H , is 10^{-3} m. The width and length of the cell are W and L , respectively. The inlet (L_{in}) and outlet (L_{out}) sections are both impermeable to the solutes and to the solvent.

The feed stream is separated into two streams: the retentate stream which is richer in the charged species, and the permeate stream which is richer in the solvent. The membrane has a negative zeta potential (ranging between $\phi_w = -1\text{mV}$ and $\phi_w = -10\text{mV}$ [13]) and a resistance

of $5.714 \times 10^{12} \text{ m}^{-1}$. The feed stream is a diluted ionic solution ($C_0^+ = 1 \times 10^{-5} \text{ mol m}^{-3}$ and $C_0^- = 1 \times 10^{-5} \text{ mol m}^{-3}$).

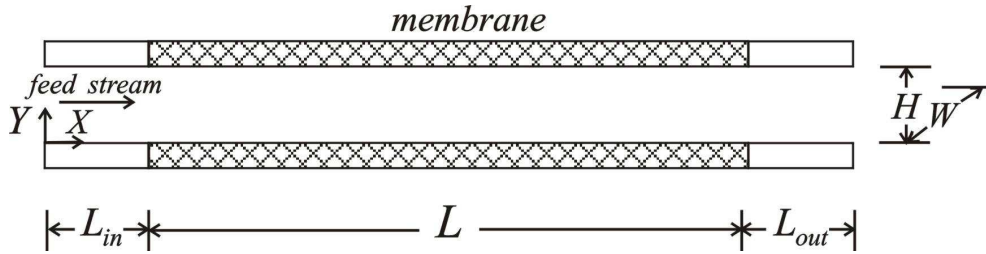


Figure 6.1 - Cell.

6.3. Theory

To model the flow and mass transport in the cell, the following simplifications were considered:

- The solutes are completely rejected by the membrane;
- The osmotic pressure can be neglected;
- The physical properties are constant (viscosity of the solution and diffusivity of the solutes);
- The electric field is determined based on the Boltzmann distribution of charged components. Effects of convection in the electric field are considered negligible;
- Electric effects on the flow are neglected.

To study the effect of the electric interactions in the concentration at the membrane surface, it is necessary to determine the electric field, the concentration field and the flow field. Therefore, the Poisson-Boltzmann, the Navier-Stokes equations and the Nernst-Planck equation were solved. Although only steady state results are presented, the numerical method is based on the solution of the transient equations. The equations were solved in the numerical domain represented in Figure 6.2. The numerical domain represents half of the physical cell (the cell is symmetric) and comprises an inlet section, an outlet section and the membrane.

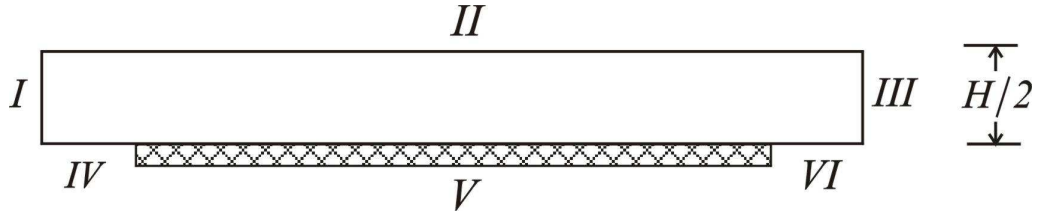


Figure 6.2 - Numerical domain.

6.3.1. Electric potential equation

The electric potential follows the Poisson-Boltzmann equation:

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) + \Pi_2 r_e \quad (6.1)$$

where ϕ is the electric potential normalized by the membrane potential (Φ_w), r_e is the ionic concentration and Π_2 is defined by:

$$\Pi_2 = \frac{FC_0 H^2}{\varepsilon M \Phi_w} \quad (6.2)$$

where F is the Faraday constant, C_0 the feed concentration, M the mean molar mass of the species in solution and ε the permittivity.

The normalized ionic concentration is the algebraic sum of the individual ionic concentrations:

$$r_e = \sum_{i=1}^N z_i c_i \quad (6.3)$$

where z_i is the electric charge number and c_i the normalized (by the feed concentration) concentration of component i .

Considering the approximation of negligible convection in both directions (X and Y), the normalized concentration of the components is related to the electric field through the Boltzmann distribution:

$$c_i = c_0 \exp[-z_i \Pi_3 (\phi - \phi_0)] \quad (6.4)$$

where c_0 is the normalized concentration of the component in the bulk (far from the membrane), ϕ_0 the non-dimension electric potential in the bulk, and Π_3 a dimensionless number defined by:

$$\Pi_3 = \frac{F\Phi_w}{RT} \quad (6.5)$$

Combining equation (6.3) and equation (6.4), the normalized ionic concentration can be related with the electric field by:

$$r_e = -2 \sinh[\Pi_3 (\phi - \phi_0)] \quad (6.6)$$

Combining all the previous equations, the Poisson-Boltzmann becomes:

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) - 2 \Pi_2 \sinh[\Pi_3 (\phi - \phi_0)] \quad (6.7)$$

To solve the Poisson-Boltzmann equation by numerical methods, boundary conditions must be specified at the boundaries of the domain. At the membrane surface ($z = 0$), non-dimensional electric potential is:

$$\phi_w = \frac{\Phi_w}{\Phi_w} = 1 \quad (6.8)$$

At the axis of symmetry the variation of the non-dimensional electric potential along the normal direction is equal to zero:

$$\frac{\partial \phi}{\partial y} = 0 \quad (6.9)$$

At the cell inlet and at the cell outlet the variation of the non-dimensional electric potential along the normal direction is also equal to zero:

$$\frac{\partial \phi}{\partial x} = 0 \quad (6.10)$$

The Poisson-Boltzmann was solved by a finite difference method. The second derivatives were approximated by implicit central differences and the non-linear term was taken explicitly.

6.3.2. Flow equations

The flow is described by the Navier-Sokes equations. For a bi-dimensional cell, the Navier-Sokes equation can be written for secondary variables (vorticity, ω , and stream function, ψ) as the vorticity transport equation and a Poisson equation. For Cartesian coordinates (x and y), the vorticity transport equation is:

$$\frac{\partial \omega}{\partial t} + v_x \frac{\partial \omega}{\partial x} + v_y \frac{\partial \omega}{\partial y} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) - \Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) \quad (6.11)$$

where Π_1 is a non - dimensional number given by:

$$\Pi_1 = \frac{FC_0 \Phi_w}{M \rho V_0^2} \quad (6.12)$$

where ρ is the fluid density and V_0 the feed velocity.

The Reynolds number (Re), based on the height of the parallel plate cell, is given by:

$$\text{Re} = \frac{\rho V_0 H}{\mu} \quad (6.13)$$

Considering that the variation of the electric potential along the horizontal direction is negligible and that r_e changes slowly along x , as first approximation, the electric term of the vorticity equation can be neglected:

$$-\Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) = 0 \quad (6.14)$$

The Poisson Equation for the stream function is:

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \quad (6.15)$$

The velocity components are related to the stream function by:

$$v_x = \frac{\partial \psi}{\partial y}; \quad v_y = -\frac{\partial \psi}{\partial x} \quad (6.16)$$

When the osmotic pressure of the solution can be neglected, the velocity boundary condition at the membrane surface is:

$$v_z = \frac{\Delta P_0}{R_m V_0 \mu_p} \quad (6.17)$$

where ΔP_0 is the transmembrane pressure and V_0 the feed velocity. The remaining boundary conditions and the numerical methods to solve the vorticity transport equation and the Poisson equation are presented in [10].

6.3.3. Mass transport equations

The mass transport equation, for each component, is:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(v_x c_i)}{\partial x} + \frac{\partial(v_y c_i)}{\partial y} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) + \left[\frac{\partial \left(\frac{z_i \Pi_3}{\text{Pe}_i} c_i \frac{\partial \phi}{\partial x} \right)}{\partial x} + \frac{\partial \left(\frac{z_i \Pi_3}{\text{Pe}_i} c_i \frac{\partial \phi}{\partial y} \right)}{\partial y} \right] \quad (6.18)$$

where Pe_i is the Peclet number:

$$\text{Pe}_i = \frac{V_0 H}{D_i} \quad (6.19)$$

In this definition D_i is the diffusivity of component i .

The electric and convective terms of equation (6.18) can be grouped:

$$\frac{\partial c_i}{\partial t} + \frac{\partial \left[\left(v_x - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial x} \right) c_i \right]}{\partial x} + \frac{\partial \left[\left(v_y - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial y} \right) c_i \right]}{\partial y} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (6.20)$$

Defining the following variables:

$$\hat{v}_x = \left(v_x - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial x} \right) \quad (6.21)$$

$$\hat{v}_y = \left(v_y - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial y} \right) \quad (6.22)$$

equation (6.20) can be simplified:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(\hat{v}_x c_i)}{\partial x} + \frac{\partial(\hat{v}_y c_i)}{\partial y} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (6.23)$$

The terms $\frac{\partial(\hat{v}_x c_i)}{\partial x}$ and $\frac{\partial(\hat{v}_y c_i)}{\partial y}$ are pseudoconvective terms that, from the numerical point of view, can be solved by methods designed to solve convection terms. The mass transport equation was solved by a fractional-step method [14], with the pseudoconvective terms separated from the diffusive terms:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(\hat{v}_x c_i)}{\partial x} + \frac{\partial(\hat{v}_y c_i)}{\partial y} = 0 \quad (6.24)$$

$$\frac{\partial c_i}{\partial t} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (6.25)$$

Equations (6.24) and (6.25) were discretized by a finite volume method. In each control volume the mass balance is:

$$F_{y_{up}} + F_{x_{left}} = F_{y_{down}} + F_{x_{right}} + \frac{dm}{dt} \quad (6.26)$$

where the letter F is used to represent the mass fluxes, Figure 6.3, and m is the mass of fluid in the finite volume.

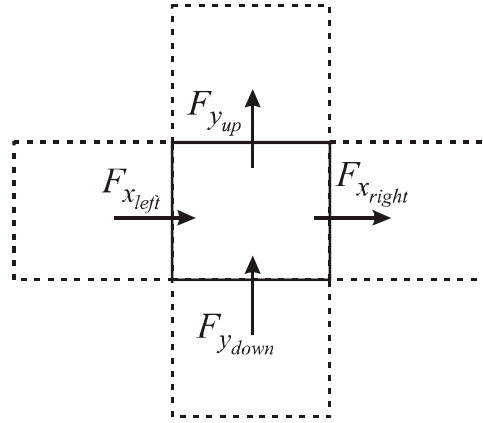


Figure 6.3 - Mass fluxes across the boundaries of a finite volume.

The convective flux (F_c) is defined by:

$$F_c = vc_i \quad (6.27)$$

and the diffusive flux by:

$$F_d = -D_i \frac{\partial c_i}{\partial y} \quad (6.28)$$

To assure mass conservation, the pseudoconvective terms were discretized by the donor-cell upwind method [14].

Boundary conditions were introduced in the discretized equations of the finite volumes by considering the appropriate boundary fluxes or concentrations. At the membrane surface, the pseudoconvective flux at the membrane surface is zero:

$$F_{y_{down}} = 0 \quad (6.29)$$

and the pseudoconvective flux at the symmetric axis is also zero:

$$F_{y_{up}} = 0 \quad (6.30)$$

At the cell inlet the normalized concentration of both components are equal to 1:

$$c_i = 1 \quad (6.31)$$

and, at the cell outlet, the variation of the normalized concentration is equal to zero:

$$\frac{\partial c_i}{\partial x} = 0 \quad (6.32)$$

At membrane surface the diffusive flux down is equal to zero:

$$F_{y_{down}} = 0 \quad (6.33)$$

as well as the diffusive flux up at the symmetric axis:

$$F_{y_{up}} = 0 \quad (6.34)$$

The diffusive flux left at cell inlet is also equal to zero

$$F_{x_{left}} = 0 \quad (6.35)$$

as well as the diffusive flux right at cell outlet:

$$F_{x_{right}} = 0 \quad (6.36)$$

6.3.4. Validation of the numerical code

The numerical code developed to solve the mass transport equation is a new code that needs to be validated. The validation can be accomplished by comparing the solution

obtained with the code for a cell with stagnant fluid with the theoretical prediction given by the Boltzmann equation. The concentration profile, given by the Boltzmann equation, is:

$$c_i = c_0 \exp[-z_i \Pi_3 (\phi - \phi_0)] \quad (6.37)$$

6.3.5. Grid optimization

Grid tests were performed to select the best grid to perform the simulations (Figure 6.4). The result obtained for grid 81×671 is almost the same as the one obtained for the grid 81×1281 . Therefore, error associated with a grid with 81×641 nodes is very small and so this was the grid selected.

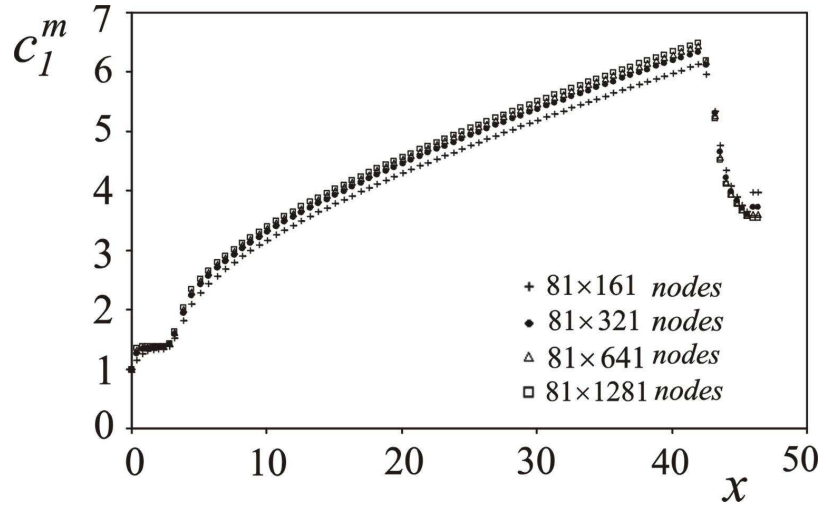


Figure 6.4 - Normalized concentration along the membrane surface for several grids for $Pe = 1 \times 10^5$, $\Delta P_0 = 1 \times 10^4$ Pa, $V_0 = 5.7 \times 10^{-3} \text{ m.s}^{-1}$, $\Pi_2 = 1.36 \times 10^6$, $\Pi_3 = 0.39$, $\Phi_w = -10$ mV and $z = 1$.

6.3.6. Convergence

The study of the convergence of the numerical method was based on the error in the concentration of the solutes in a critical node of the cell. The critical node is located near the cell exit, where the convergence is slower. The error of the concentration in the critical node was determined by:

$$\varepsilon_{crit} = \left| \frac{C_{crit}^k - C_{crit}^{k-1}}{C_{crit}^k} \right| \quad (6.38)$$

where *crit* refers to the critical node and *k* to the current iteration.

An example of the study of the convergence is presented in Figure 6.5. The normalized concentration converges to a constant value. The iterative process stops when the following criterions were observed:

$$\varepsilon_{crit} < 10^{-3} \quad (6.39)$$

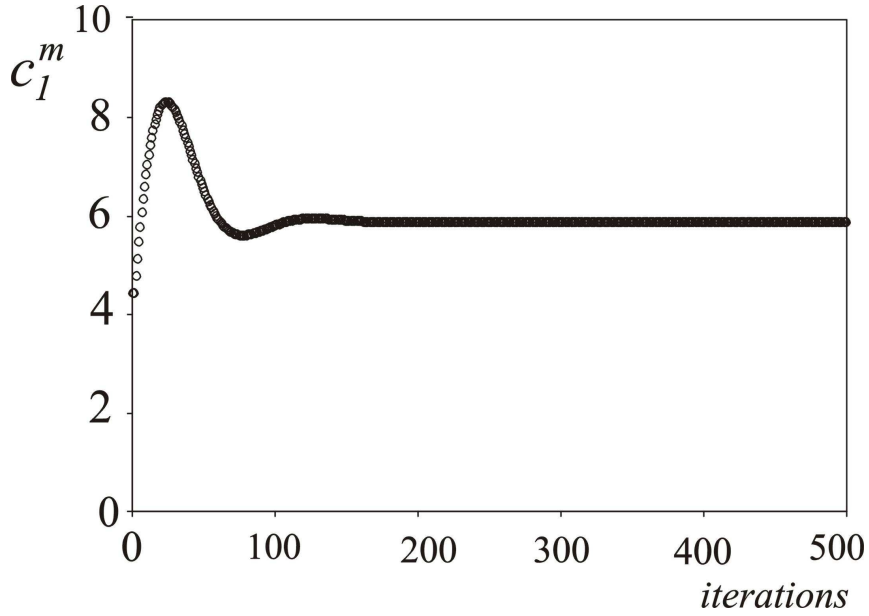


Figure 6.5 - Normalized concentration in a critical node near the end of the cell versus the number of iterations for $Pe = 1 \times 10^5$, $\Delta P_0 = 1 \times 10^4$ Pa, $V_0 = 5.7 \times 10^{-3} \text{ m.s}^{-1}$, $\Pi_2 = 1.36 \times 10^6$, $\Pi_3 = 0.39$,

$$\Phi_w = -10 \text{ mV and } z = 1.$$

6.4. Results and discussion

The electric potential equation was solved to determine the electric field in the membrane cell. The results, for two values of the membrane potential are in Figure 6.6. The data show that the membrane disturbs the electric field along a short distance of $0.05 H$.

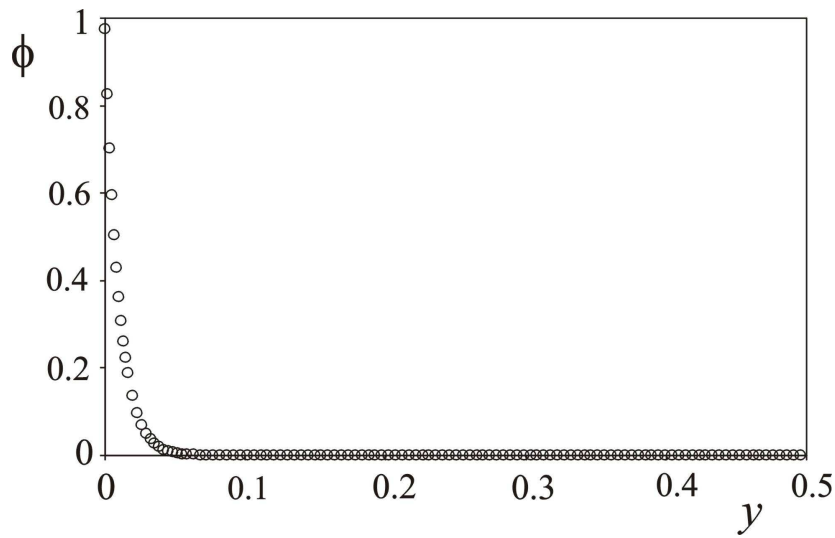


Figure 6.6 - Normalized potential along the direction normal to the membrane for $\Pi_2 = 1.36 \times 10^6$ and $\Pi_3 = 0.39$.

The introduction of the electric field requires the validation of the numerical method implemented. The numerical method was validated by comparing data obtained for a stagnant fluid with the Boltzmann equation. The comparison is shown in Figures 6.7 and 6.8. The results obtained by the numerical method are accurate, even for large membrane potentials.

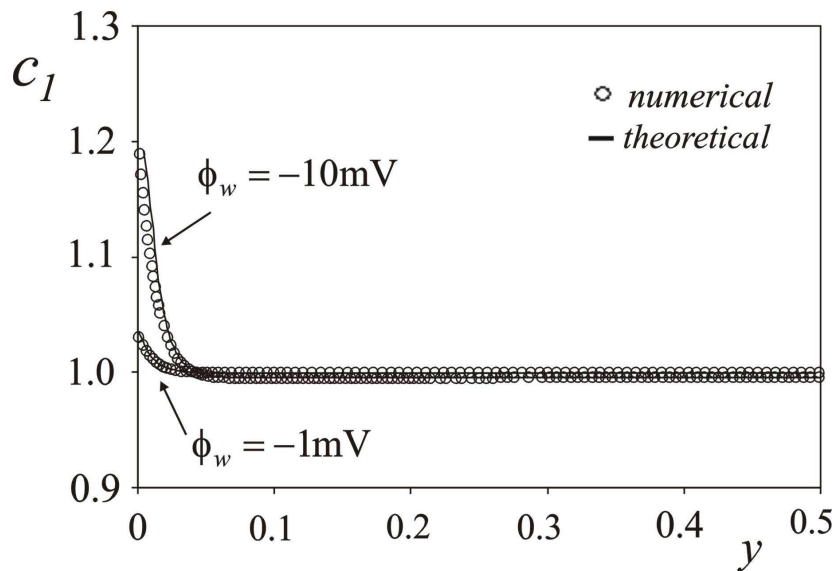


Figure 6.7 - Normalized concentration along the vertical direction of the species with a positive charge in a cell containing stagnant fluid for $\Pi_2 = 1.36 \times 10^6$ and $\Pi_3 = 0.39$.

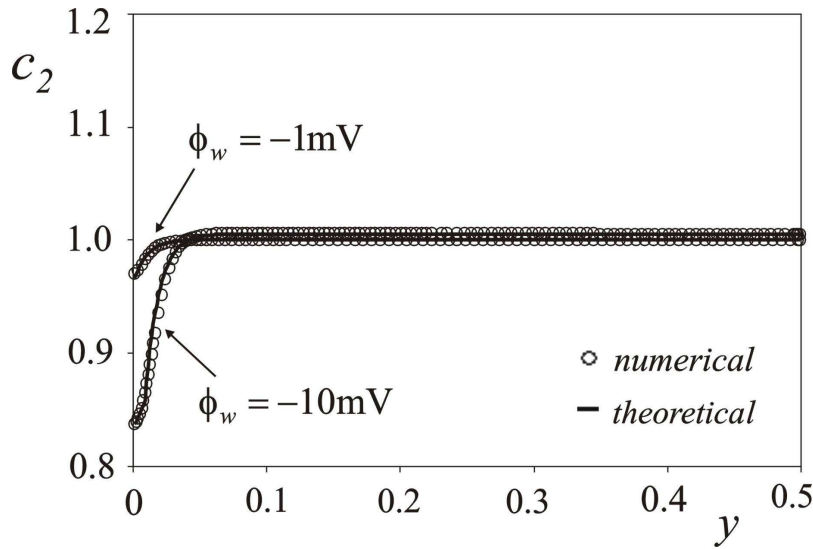


Figure 6.8 - Normalized concentration along the vertical direction of the species with a negative charge in a cell containing stagnant fluid for $\Pi_2 = 1.36 \times 10^6$ and $\Pi_3 = 0.39$.

The separation process was studied considering two membrane cells: a neutral membrane cell and a negatively charged membrane cell. The results are in Figure 6.9. Figure 6.9 shows that the concentration along the membrane is higher when the membrane and the component have opposite charges and lower when the membrane and the component have the same charge. Both components have the same intermediate concentration in the cell with a neutral membrane.

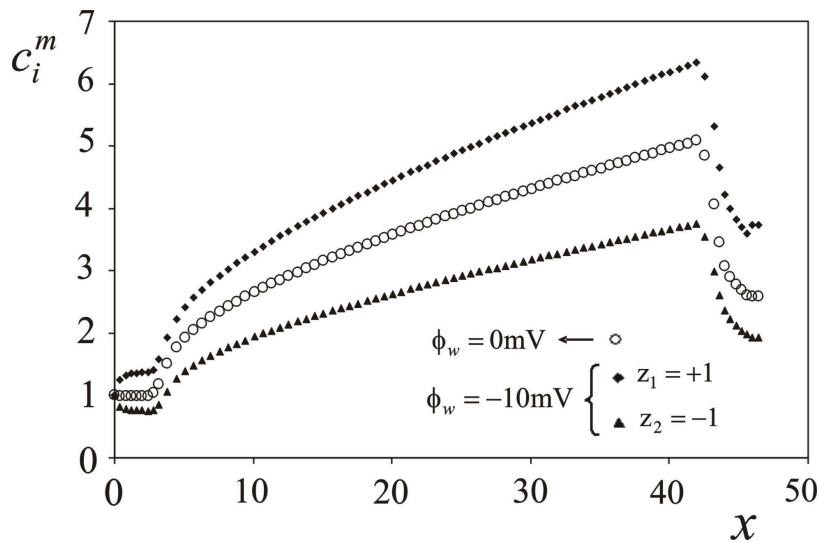


Figure 6.9 - Concentration along the membrane for $Pe = 1 \times 10^5$, $\Delta P_0 = 1 \times 10^4$ Pa, $V_0 = 5.7 \times 10^{-3} \text{ m.s}^{-1}$, $\Pi_2 = 1.36 \times 10^6$, $\Pi_3 = 0.39$, $\Phi_w = 0 \text{ mV}$ and $\Phi_w = -10 \text{ mV}$ ($z_1 = 1$ and $z_2 = -1$).

6.5. Conclusions

The Poisson-Boltzmann, the Nernst-Planck equation and the Navier-Stokes equations were solved by numerical methods to study the mass transport of charged species in the vicinity of a charged membrane. The fractional-step method used to solve the mass transport equation is sufficiently adequate and easy to implement. The donor-cell upwind method used to discretize the convective terms of the mass transport equation assures mass conservation. The method to solve the mass transport equation was validated by comparing the numerical solution for a membrane cell containing stagnant fluid with the Boltzman equation.

The code developed was used to study the mass transfer of two charged species in the vicinity of a semi-permeable negatively charged membrane. As it was expected, the ion with positive charge accumulates, in a higher quantity, near the membrane.

Further work is necessary to improve the code developed. In the future we intend to solve the full vorticity equation, including electric terms neglected in this work. The electric potential equation will be solved considering the effect of convection in the charged species distribution. Finally, the code will be improved to include a higher number of charged species, an improvement that will allow the study of protein fractionation.

6.6. Nomenclature

C_i	Solute concentration of component i
c_i	Normalized solute concentration of component i
C_0	Ionic feed/bulk concentration
c_0	Normalized ionic feed/bulk concentration
C_0^+	Concentration of the positively charged component
C_0^-	Concentration of the negatively charged component
C_i^m	Concentration of component i at membrane surface
c_i^m	Normalized solute concentration of component i at membrane surface
C_{crit}^k	Concentration on a critical location
D_i	Molecular diffusivity of component i

F	Faraday constant
F_c	Convective mass flux
F_d	Diffusive mass flux
$F_{y_{down}}$	Mass flux across the lower boundary of a finite volume
$F_{y_{up}}$	Mass flux across the upper boundary of a finite volume
$F_{x_{left}}$	Mass flux across the left boundary of a finite volume
$F_{x_{right}}$	Mass flux across the right boundary of a finite volume
H	Distance between parallel plates
k	Current time step
L_{out}	Length of the outlet section
L_{in}	Length of the inlet section
L_m	Total length of the membrane
L	Length of the cell
M	Molar mass
R	Gas constant
r_e	Normalized ionic concentration
R_m	Membrane resistance
T	Temperature
t	Non-dimensional time
V_0	Mean feed velocity
V_x	Longitudinal component of the velocity
v_x	Normalized longitudinal component of the velocity
$\hat{v}_x$	Normalized pseudovelocity (component x)
V_y	Vertical component of the velocity
v_y	Normalized vertical component of the velocity
$\hat{v}_y$	Normalized pseudovelocity (component y)
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Y	Vertical coordinate
y	Normalized vertical coordinate
W	Width of the cell
z_i	Charge of component i

Non-dimensional numbers

Pe_i	Peclet number of component i
Re	Reynolds number
Π_1	Non-dimensional number defined by equation (6.12)
Π_2	Non-dimensional number defined by equation (6.2)
Π_3	Non-dimensional number defined by equation (6.5)

Greek Symbols

ΔP_0	Static pressure difference across the permeable membrane
ε	Permittivity
ε_{crit}	Numerical error of the concentration on a critical location
ψ	Stream function
ω	Vorticity
ρ	Density
μ	Viscosity
Φ	Electric potential
ϕ	Non-dimensional electric potential
Φ_0	Electric potential of the bulk
ϕ_0	Normalized electric potential of the bulk
Φ_w	Membrane electric potential
ϕ_w	Normalized membrane electric potential

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Chapter 7

Interaction between the electric and concentration fields in the fractionation of two macromolecules using a hybrid membrane cell – CFD study

The numerical study of membrane separation processes with electric interactions requires the simultaneous solution of Poisson-Boltzmann, Navier-Stokes and Nernst-Planck equations. These equations are solved considering the contribution of the electric interactions. A numerical method was developed, and implemented, to deal with the coupling between the electric field, the flow field and the concentration fields of the ionic species in solution. The convergence was obtained and the numerical method was validated. For a binary ionic solution, the results are similar to those obtained with a simplified method [1] which assumes the Boltzmann distribution of the ionic species. For high molecular diffusivity of the components, the convection is negligible, relatively to the diffusion, and the numerical solution is similar to the one obtained for a stagnant fluid.

The numerical code developed is applied to the study of macromolecules fractionation in an ionic solution, through a Hybrid Membrane Cell composed by negatively charged semi-permeable membranes (impermeable to the solutes) and neutral fully-permeable membranes, alternating in series. The normalized concentration profiles of the species along the normal and tangential directions were obtained, as well as the non-dimensional electric potential along the normal direction. When the component with the highest diffusivity has the same charge of the semi-permeable membrane, the separation, in the vicinity of this membrane, improves. However, due to the interactions between the electric and the concentration fields, in the region crossed by the streamlines of the concentrate stream, the separation in the fully permeable membranes is worsened.

The contents of this chapter were adapted from: S.I.S. Pinto, J.M. Miranda, J.B.L.M. Campos, Interactions between the electric and concentration fields in the fractionation of two macromolecules using a hybrid membrane cell – CFD study, *Desalination and Water Treatment* (2011) in Press.

7.1. Introduction

The authors of the present paper have been exploring the potential of different types of Hybrid Membrane Cells (HMC) [2, 3] to fractionate macromolecules. Generically, an HMC [2, 3] is composed by two kinds of membranes alternating in series: a semi-permeable membrane and a fully-permeable membrane.

The first study [2] was about a HMC with a semi-permeable membrane only permeable to the solvent, and a fully-permeable membrane permeable to both solutes and solvent. The macromolecules separation is done by differential diffusivity. The solute with lower diffusivity remains concentrated near the semi-permeable surface while the solute with higher diffusivity leaves the membrane surface into the bulk. The solute with lower diffusivity, accumulated at the semi-permeable surface, is, preferentially, recovered at the fully-permeable membrane. Therefore, the outflow stream of the cell is rich in the solute with higher diffusivity (Figure 7.1) [2].

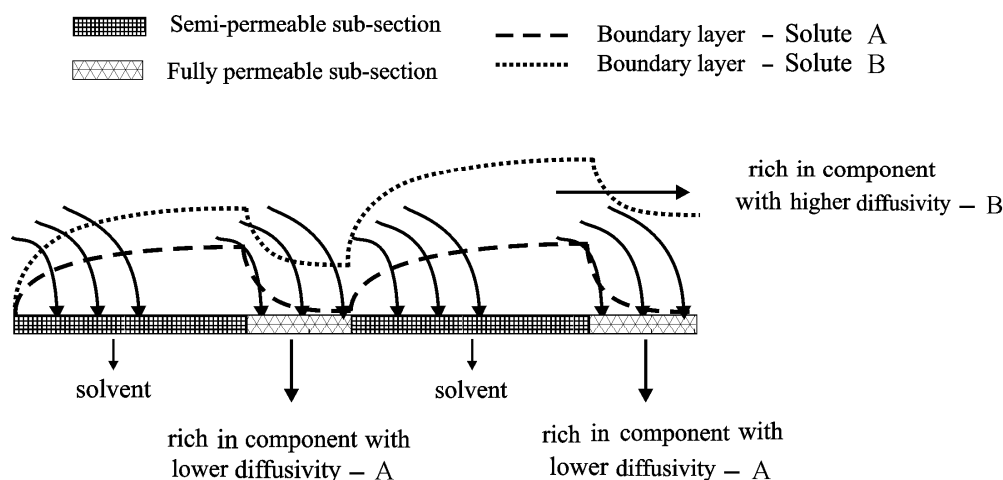


Figure 7.1 – Differential diffusivity in a Hybrid Membrane Cell.

The second study was about a HMC [3] in which both solutes are transmitted through the semi-permeable membrane, depending on their macromolecules sizes. In this type of HMC, the macromolecules with a size lower than the size of the pores cross preferentially the semi-permeable membrane. The permeate stream leaving this section is then rich in these macromolecules. The solute with macromolecules higher than the size of the pores is retained and leaves the cell, preferentially, through the fully-permeable membranes. This

solute has also the lower molecular diffusivity, remaining close to the semi-permeable membranes, a factor that increases the efficiency of the separation.

However, the potential of a HMC can be further explored. Electrical effects were not taken into account in previous works. The careful selection of the charge of the membranes could contribute to optimize the performance of the cells. Further work is needed to understand the effect of the electrical effects on the separation.

The electrical interactions between the membrane and the charged components in the polarized boundary layer are usually neglected in most of the studies [4, 5]. Some attempts have been made to include them in analytical [6-8] and numerical studies [9]. Analytical studies of mass transport in the polarized boundary layer are usually based on the stagnant film model and are not suitable for complex problems involving concentration dependent properties, solutions containing multiple ionic species and membranes with non-uniform zeta potentials. Numerical methods have been applied to the transport in pores [10, 11] or to stagnant boundary layers [9]. Related electrochemical problems have been studied in other areas of research, namely electroosmotic flows [12-17]. However, these systems do not combine, as membrane separation processes do, electrochemical transport with tangential and normal convection and concentration polarization.

To study the electric interactions between membrane and components, the Poisson-Boltzmann, the Navier-Stokes and the Nernst-Planck equations need to be solved. In a previous work [1], these set of equations were solved by a simplified approach. A binary ionic solution was considered and the effect of convection on the ionic distribution was neglected. This simplification removed the coupling between the Poisson-Boltzmann and the Nernst-Planck equations, and the electric potential was determined in a simplified way from the Boltzmann distribution of the charged ions. Moreover, the electric terms of the Navier-Stokes equations were also neglected [1]. However, in practice, most systems have a large number of ionic species and the tangential velocity near the membrane has an important contribution to the mass transport in the cell.

In the present study, the Poisson-Boltzmann, the Navier-Stokes and the Nernst-Planck equations were solved without any simplification. A numerical method was developed to deal with the coupling between the electric and concentration fields of all the species in

solution. Both mass transport equations and flow equations have the electric terms incorporated.

The new numerical code developed will be applied to the fractionation of two macromolecules with opposite charges in an ionic solution of NaCl, using a HMC composed by negatively charged semi-permeable membranes (only permeable to the solvent) and neutral fully-permeable membranes (permeable to all components and to the solvent), alternating in series. Additionally to the diffusion mechanisms, already studied by Pinto et al. [2], the importance of the electric interactions in this type of separation is analyzed in this work.

7.2. Cell description

The HMC under studied is composed by n membrane sections, where each membrane section has a semi-permeable membrane with a zeta potential Φ_w^s , only permeable to the solvent, and a neutral fully-permeable membrane, permeable to all components (Figure 7.2).

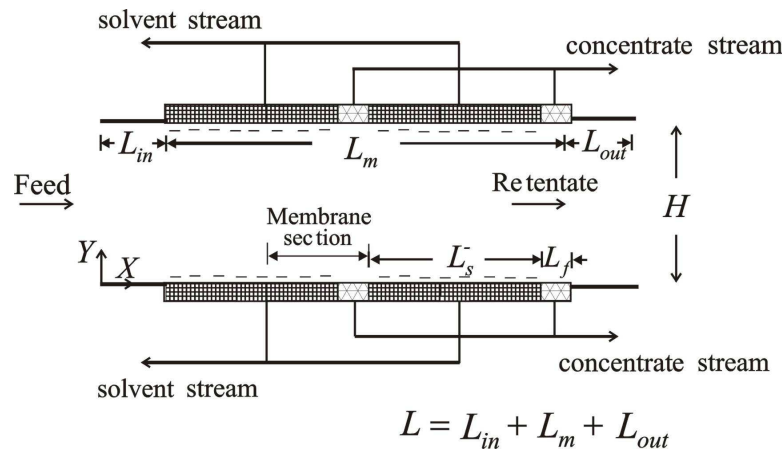


Figure 7.2 – Hybrid Membrane Cell composed of negatively charged semi-permeable membranes and neutral fully permeable membranes.

In the separation process, the feed stream is separated into three streams: the retentate stream, which leaves the cell through the principal channel, the permeate stream (solvent stream) and the concentrate stream. The solvent is the only component crossing the semi-permeable sub-sections. All the species in solution leave the cell through the neutral fully-

permeable sub-sections, which are permeable to all components and to the solvent (concentrate stream).

The characteristics of the conventional cell (CC), with only one semi-permeable membrane, and the characteristics of the HMC, both used in this study, are listed in Table 7.1. The operational conditions are also presented in this table.

Table 7.1 - Characteristics of the Conventional Cell (CC) and Hybrid Membrane Cell (HMC).

Membrane	CC OMEGA	HMC OMEGA
	Polysulfone membrane	Polysulfone membrane
R_m	$5.714 \times 10^{12} \text{ m}^{-1}$	$5.714 \times 10^{12} \text{ m}^{-1}$
H	0.001 m	0.001 m
L_m	0.250 m	0.2778 m
L_s^-	0.250 m	0.125 m
L_f	—————	0.0139 m
$\varepsilon_f^{[a]}$	—————	10 %
n_{sec}	1	2
$\sum_{k=1}^n L_{s,k}^-$	0.250 m	0.250 m
$\sum_{k=1}^n L_{f,k}$	—————	0.0278 m
$L_{in} = L_{out}$	0.02 m	0.02 m
ΔP_0	$1 \times 10^4 \text{ Pa}$	$1 \times 10^4 \text{ Pa}$

$$^{[a]} \varepsilon_f = \frac{L_f}{L_f + L_s^-} \times 100$$

7.3. Characterization of the inlet feed and general assumptions

Inlet feed:

- A mixture of two macromolecules, M_1 and M_2 , with opposite charges, in an ionic solution of NaCl (Na^+ and Cl^-);

- All the species have the same molar concentration ($C_{M,i}^0$) and the solution is electrically neutral, since the sum of the inlet ionic concentrations of all the species is equal to zero.

General assumptions:

- The semi-permeable membrane is considered to be permeable to the solvent but completely impermeable to the solutes;
- The osmotic pressures of the macromolecules, M_1 and M_2 , and of the ionic species, Na^+ and Cl^- , are considered negligible, since the concentrations of these species are, everywhere in the cell including over the semi-permeable membranes, very low (dilute solution);
- The transport properties (viscosity and diffusivity) of all the species are considered constant. In a very diluted solution, viscosity and diffusivity are practically independent of the concentration of the species, including at the membrane surface [18-20];
- The viscosity of the solution is considered identical to that of pure water everywhere inside the cell (very diluted solution);
- Electric effects inside the membrane are not considered;

The properties of the components used are represented in Table 7.2.

Table 7.2 – Properties of the components M_1 and M_2 in an ionic solution of NaCl.

Component	M_1	M_2	Na^+	Cl^-
M_i (kg/kmol)	69000	10000	23	35.45
z_i	+2	-2	+1	-1
Pe_i	1.37×10^6	8.00×10^4	7.14×10^4 [19]	4.68×10^4 [19]
Re	100	100	100	100
C_i^0 (kg/m ³)	6.9×10^{-5}	1.0×10^{-5}	2.30×10^{-8}	3.545×10^{-8}
$C_{M,i}^0$ (kmol/m ³)	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}

7.4. Numerical method

In order to study the effect of the electric interactions, it was necessary to determine the electric, the concentration and the flow fields. The Poisson-Boltzmann, the Nernst-Planck and the Navier-Stokes equations were then solved by numerical methods (CFD).

7.4.1. Domain

The equations were solved in the numerical domain represented in Figure 7.3; Figure 7.3a) shows the domain of a conventional cell with a semi-permeable membrane; and Figure 7.3b) the domain of the HMC represented in Figure 7.2. Since the cell is symmetric, the numerical domain encloses half of the cell and comprises an inlet section, an outlet section and the membrane sub-sections.

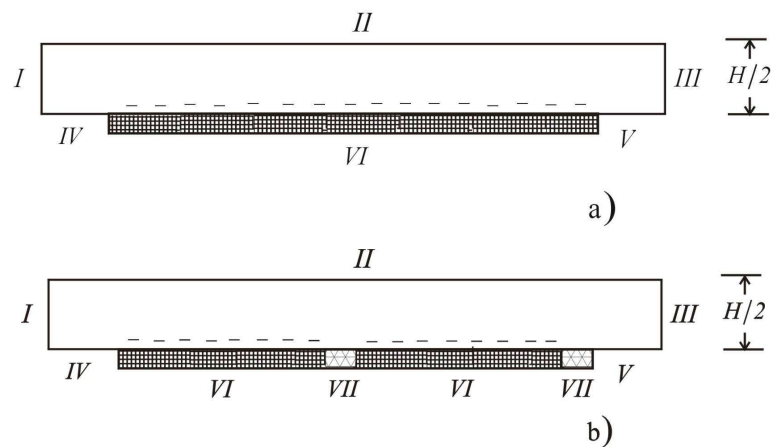


Figure 7.3 – Schematic representation of the domain: a) conventional cell (CC) b) hybrid membrane cell (HMC) and respective boundaries (I – cell inlet; II – symmetric axis; III – cell outlet; IV – wall; V – wall; VI – semi-permeable membrane with negative zeta-potential; VII – fully-permeable membrane with zeta-potential equal to zero).

7.4.2. Conservative equations

For a better understanding, from now on, all the lowercase variables symbolize normalized variables: the non-dimensional electric potential is normalized by the absolute value of the semi-permeable membrane potential (Φ_w), the concentrations by the inlet concentrations of the solutes, the velocities by the inlet velocity and the geometric

dimensions by the height of the cell. The uppercase variables symbolize dimensional variables.

7.4.2.1. Electric potential equation

Assuming that the ions in solution can be considered point charges, the electric potential follows the Poisson-Boltzmann equation:

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) + \Pi_2 r_e \quad (7.1)$$

where ϕ is the normalized electric potential, r_e the sum of the ionic concentrations of all the components and Π_2 a non-dimensional number defined by:

$$\Pi_2 = \frac{FC_{ref}^0 H^2}{\varepsilon M_{ref} \Phi_w} \quad (7.2)$$

where F is the Faraday constant, C_{ref}^0 the concentration of the reference component in the bulk, M_{ref} the molar mass of the reference component and ε the permittivity. The cation of the solution, Na^+ , was arbitrarily chosen as the reference component:

$$C_{ref}^0 = C_{\text{Na}^+}^0 \quad (7.3)$$

$$M_{ref} = M_{\text{Na}^+} \quad (7.4)$$

The sum of the normalized ionic concentrations was determined according to the local ionic concentrations:

$$r_e = \sum_{i=1}^N z_i \frac{C_i^0}{C_{ref}^0} \frac{M_{ref}}{M_i} c_i \quad (7.5)$$

where z_i is the electric charge, c_i the normalized concentration of the component i and M_i the molar mass of component i .

The electric potential equation (7.1) was solved by a fractional-step method with the diffusive terms separated from the independent term. Firstly, equation (7.6), with the independent term, was solved by direct integration. In a second step, equation (7.7), with the diffusive terms of the electric potential equation, was solved through a finite difference method. The second derivatives were approximated by central differences and the discretized equations were solved by an implicit method.

$$\frac{\partial \phi}{\partial t} = \Pi_2 r_e \quad (7.6)$$

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) \quad (7.7)$$

The boundary conditions of the domain to solve the electric potential equation are listed below:

- At the surface of the semi-permeable and fully-permeable membranes ($y = 0$), the non-dimensional electric potential is equal to the ratio between the potential at the membrane surface and the potential (absolute value) of the semi-permeable membrane:

$$\phi = \frac{\Phi(y=0)}{\Phi_w} \quad (7.8)$$

- At the axis of symmetry, the non-dimensional electric potential is equal to zero:

$$\phi = 0 \quad (7.9)$$

- At the cell inlet and at the cell outlet, the non-dimensional electric potential is also equal to zero:

$$\phi = 0 \quad (7.10)$$

- At the wall of the cell (impermeable areas), the variation of the non-dimensional electric potential along the normal direction is equal to zero:

$$\frac{\partial \phi}{\partial y} = 0 \quad (7.11)$$

7.4.2.2. Flow equations

The flow in the cell is described by the Navier-Stokes equations. For a bi-dimensional cell, the Navier-Stokes equations can be written for secondary variables (vorticity, ω , and stream function, ψ) as the vorticity transport equation and a Poisson type equation.

For Cartesian coordinates (x and y), the vorticity transport equation is:

$$\frac{\partial \omega}{\partial t} + v_x \frac{\partial \omega}{\partial x} + v_y \frac{\partial \omega}{\partial y} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) - \Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) \quad (7.12)$$

where Π_1 is a non - dimensional number given by:

$$\Pi_1 = \frac{FC_{ref}^0 \Phi_w}{M_{ref} \rho V_0^2} \quad (7.13)$$

where ρ is the fluid density and V_0 the feed velocity. The term $-\Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right)$ accounts for the vorticity generation due the momentum induced by the electric field.

The Reynolds number (Re), based on the height of the parallel plate cell (H) and on the viscosity of the solution ($\bar{\mu}$) is given by:

$$\text{Re} = \frac{\rho V_0 H}{\bar{\mu}} \quad (7.14)$$

The Poisson Equation for the stream function is:

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \quad (7.15)$$

and the velocity components are related to the stream function by:

$$v_x = \frac{\partial \psi}{\partial y}; \quad v_y = -\frac{\partial \psi}{\partial x} \quad (7.16)$$

The convective, diffusive and independent term (electric term) of the vorticity transport equation (7.12) were discretized by an implicit method. A hybrid method combining upwind and central differences discretizations was used for the convective terms. Central differences discretizations of second order were used for the diffusive terms and for the independent term. The derivatives of equation (7.15) were approximated by second order central differences. The boundary conditions to solve the Navier-Stokes equations are presented in detail in reference [2].

7.4.2.3. Mass transport equations

The mass transport equation, Nernst-Planck equation, of each component is given by:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(\hat{v}_x c_i)}{\partial x} + \frac{\partial(\hat{v}_y c_i)}{\partial y} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (7.17)$$

where

$$\hat{v}_x = \left(v_x - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial x} \right) \quad (7.18)$$

$$\hat{v}_y = \left(v_y - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial y} \right) \quad (7.19)$$

Pe_i is the Peclet number based on the height of the parallel plate cell (H) and on the diffusivity (D_i) of component i :

$$\text{Pe}_i = \frac{V_0 H}{D_i} \quad (7.20)$$

and Π_3 is a non-dimensional number defined by:

$$\Pi_3 = \frac{F\Phi_w}{RT} \quad (7.21)$$

The terms $\frac{\partial(\hat{v}_x c_i)}{\partial x}$ and $\frac{\partial(\hat{v}_y c_i)}{\partial y}$ are pseudo-convective terms, and, from a numerical point of view, can be treated by the same method used to discretize the convective terms of the vorticity transport equation. In order to simplify the convergence and resolution of the mass transport equation, equation (7.17) was solved by a fractional-step method [1], with the pseudo-convective terms separated from the diffusive terms:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(\hat{v}_x c_i)}{\partial x} + \frac{\partial(\hat{v}_y c_i)}{\partial y} = 0 \quad (7.22)$$

$$\frac{\partial c_i}{\partial t} = \frac{1}{Pe_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (7.23)$$

Equations (7.22) and (7.23) were discretized by a finite volume method and, to assure mass conservation, the pseudo-convective terms were discretized by the donor-cell upwind method [1]. More details about the discretization and respective boundary conditions can be found in [1].

7.4.3. Iterative method

The iterative method used to solve the discretized equations is schematically represented in Figure 7.4. Starting with the initial conditions (electric potential, concentration and velocity), an iterative cycle was performed to solve the mass transport equation, the electric potential equation, the Poisson equation, and the vorticity transport equation. The velocity components were determined from the stream function definition – equation (7.16).

Electric, concentration and flow fields were studied to analyse the convergence of the numerical method. This study was based on the errors in the concentration of the solutes, in the electric potential and in the vorticity of the flow, in a critical node of the cell. This

critical node was located near the cell exit, at the end of last negatively charged semi-permeable membrane, where the convergence is very slow.

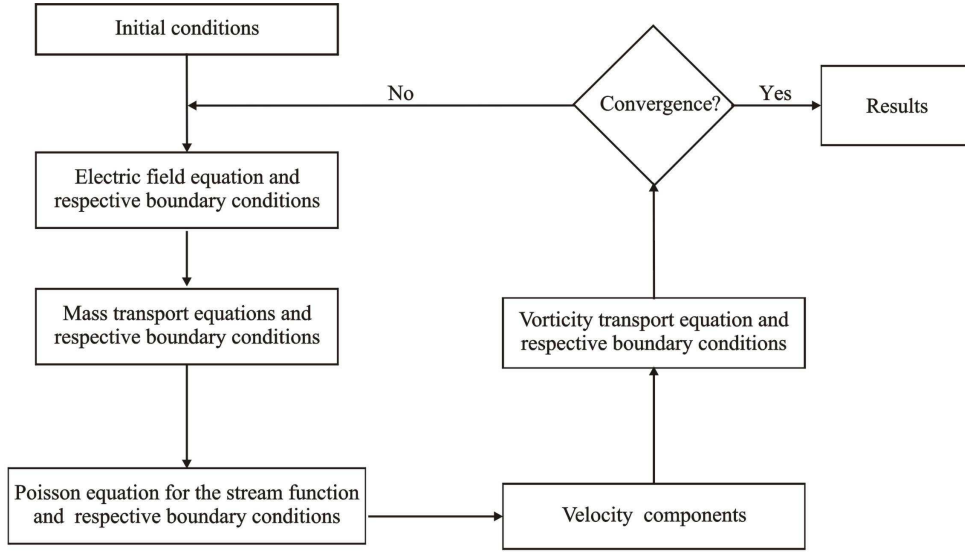


Figure 7.4 – Flowsheet describing the iterative method to solve the discretized equations.

The error of the concentration of component i in the critical node was determined by:

$$\mathcal{E}_{c i \text{ crit}} = \left| \frac{C_{i, \text{crit}}^k - C_{i, \text{crit}}^{k-1}}{C_{i, \text{crit}}^k} \right|; \quad (7.24)$$

the error of the electric potential in the same critical node was determined by:

$$\mathcal{E}_{\phi \text{ crit}} = \left| \frac{\phi_{\text{crit}}^k - \phi_{\text{crit}}^{k-1}}{\phi_{\text{crit}}^k} \right|; \quad (7.25)$$

and the error of the vorticity in the same critical node was determined by:

$$\mathcal{E}_{\omega \text{ crit}} = \left| \frac{\omega_{\text{crit}}^k - \omega_{\text{crit}}^{k-1}}{\omega_{\text{crit}}^k} \right| \quad (7.26)$$

where crit refers to the critical node and k to the current iteration.

Moreover, to assure that the numerical method converges to the correct solution, the total sum of the residues of the electric potential equation, R_ϕ , was determined by:

$$R_\phi = \sum_{g=2}^{n-1} \sum_{h=2}^{m-1} \left| \frac{\partial \phi}{\partial t} \right|_{g,h} \quad (7.27)$$

where $\left| \frac{\partial \phi}{\partial t} \right|_{g,h}$ is the time derivative of the electric potential at the node (g, h) .

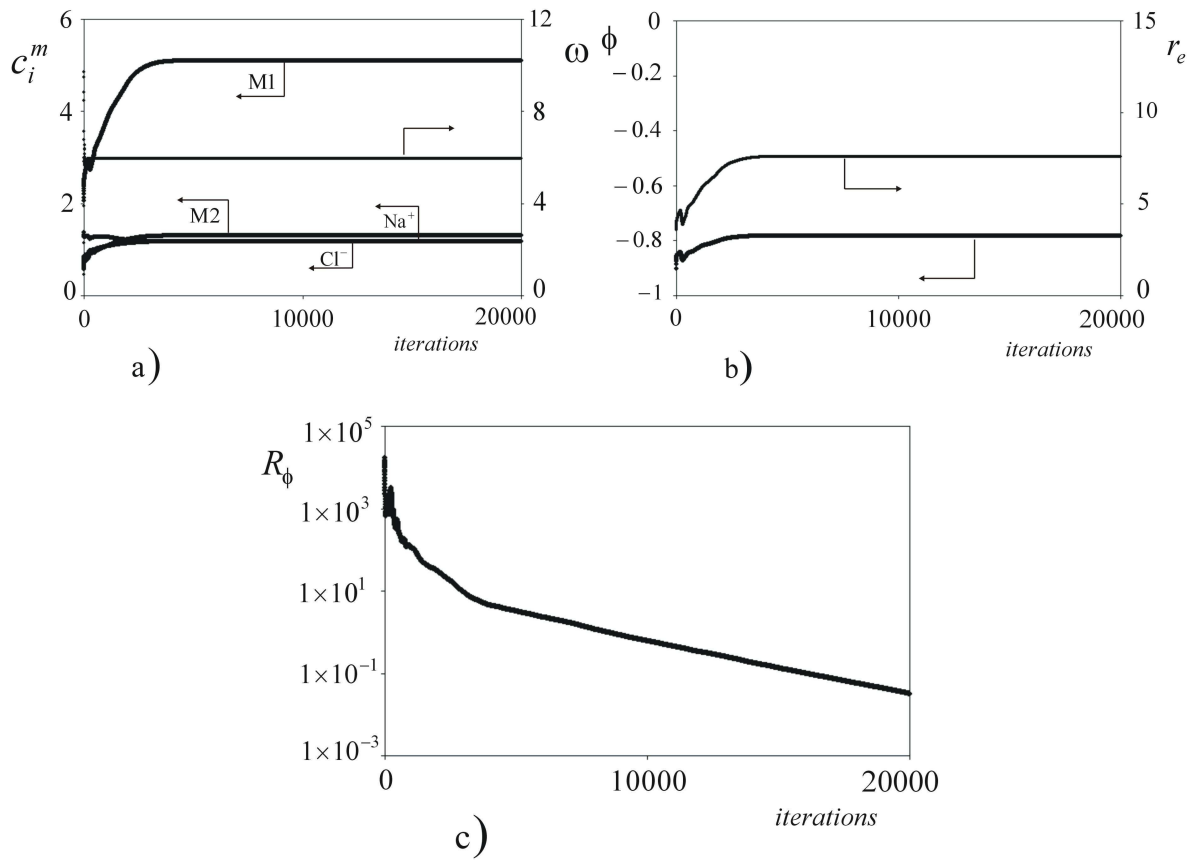


Figure 7.5 – a) Normalized concentration of the species and vorticity of the flow; b) normalized electric potential and normalized ionic concentration; c) Total residues of the electric potential equation $(C_{MI}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3, C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3, C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3, C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3, \text{Re} = 100, \text{Pe}_{MI} = 1.30 \times 10^6, \text{Pe}_{M2} = 8.00 \times 10^4, \text{Pe}_{Na^+} = 7.14 \times 10^4, \text{Pe}_{Cl^-} = 4.68 \times 10^4, \Pi_1 = 1.07 \times 10^{-4}, \Pi_2 = 1.36 \times 10^5, \Pi_3 = 0.387, \Delta P_0 = 1 \times 10^4 \text{ Pa})$.

The normalized concentration, the non-dimensional electric potential and the vorticity must converge to a constant value (Figure 7.5a and 7.5b). The total sum of the residues of the electric potential equation dependent on the concentration of the components has to decrease to a very small value (Figure 7.5c). The iterative process stops when the following criteria were observed:

$$\begin{cases} \varepsilon_{ci \text{ crit}} < 10^{-3} \\ \varepsilon_{\varphi \text{ crit}} < 10^{-3} \\ \varepsilon_{\omega \text{ crit}} < 10^{-3} \\ R_{\varphi} < 10^{-1} \end{cases} \quad (7.28)$$

Figure 7.5 is an example of the convergence of the numerical data in the separation of M_1 from M_2 , in an ionic solution of NaCl, processed in a hybrid membrane cell with diffusivity and electric mechanisms (most drastic condition used in this paper).

7.4.4. Grid optimization

Grid tests were performed to select the best grid. A special care was taken since in a HMC there is an abrupt concentration change in the boundary between semi and fully-permeable membrane sub-sections [2, 3]. The independent parameter chosen to perform these tests was the discretization error of the solute concentration expressed by:

$$\varepsilon_{\bar{c}_i^{m,s}} = \frac{\bar{c}_i^{m,s,refgrid} - \bar{c}_i^{m,s}}{\bar{c}_i^{m,s,refgrid}} \quad (7.29)$$

where $\bar{c}_i^{m,s}$ refers to the mean normalized concentration of component i at the semi-permeable membrane surface and the superscript *refgrid* refers to the reference grid. The results of the grid tests are summarized in Table 7.3 and Table 7.4.

The results (Tables 7.3 and 7.4) show that all the grids are sufficiently accurate since the error is less than 1% relatively to the reference grid. The grid of 149×501 was chosen to obtain the numerical results.

Table 7.3 – Grid tests for the normal direction y ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $\text{Re} = 100$, $\text{Pe}_{M1} = 1.30 \times 10^6$, $\text{Pe}_{M2} = 8.00 \times 10^4$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

<i>Grid</i> ($n \times m$)	$ni_m^{[b]}$	$\epsilon_{CM1}^{-m,s}$	$\epsilon_{CM2}^{-m,s}$
149×251	132	0.53 %	0.08 %
149×501	132	0.12 %	0.06 %
149×1001	132	reference grid	reference grid

^[b] ni_m is the number of grid nodes along the total length of the membrane

Table 7.4 – Grid tests for the tangential direction x ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $\text{Re} = 100$, $\text{Pe}_{M1} = 1.30 \times 10^6$, $\text{Pe}_{M2} = 8.00 \times 10^4$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

<i>Grid</i> ($n \times m$)	$ni_m^{[b]}$	$\epsilon_{CM1}^{-m,s}$	$\epsilon_{CM2}^{-m,s}$
85×501	68	0.48 %	0.31 %
149×501	132	0.12 %	0.06 %
281×501	264	reference grid	reference grid

^[b] ni_m is the number of grid nodes along the total length of the membrane

7.4.5. Comparison with previous method

The numerical method developed in the present work is an improvement of the work developed by Pinto et al. [1]. In the method developed by Pinto et al. [1], the electric term of the vorticity equation was neglected:

$$-\Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) = 0 \quad (7.30)$$

The Boltzmann distribution of ionic species:

$$c_i = c_i^0 \exp[-z_i \Pi_3 (\phi - \phi_0)] \quad (7.31)$$

was used to determine r_e . In this way, the equation of the electrical potential becomes independent of the concentration field:

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) - 2\Pi_2 \sinh[\Pi_3 (\phi - \phi_0)] \quad (7.32)$$

The electric potential was determined by solving equation (7.32). This step was followed by an iterative method to solve the flow and mass transport equations.

7.5. Results and discussion

In the work of Pinto et al. [1], the electric field was considered independent of the concentration fields and the electric term of the vorticity equation was neglected. In the present work, the electric field and the concentration fields interact and the electric term of the vorticity equation is taken into account. In the following sections, the effect of these modifications on the concentration and electric fields are going to be studied. Afterwards, a study of the mass transport in a hybrid membrane cell with electric effects will be presented.

7.5.1. Coupling mass and electric fields

The mass transport in a conventional cell with a negatively charged semi-permeable membrane was simulated to study the interaction between mass and electric fields. The feed stream is an ionic solution of NaCl (Na^+ and Cl^-) and the concentration profiles of the ionic species along the direction perpendicular to the membrane (at the end of the semi-permeable membrane) are shown in Figure 7.6 (a and b). The concentration profiles obtained by solving the coupled Poisson-Boltzmann and Nernst-Planck equations are similar to those obtained by the method developed by Pinto et al. [1]. Also shown in the figures are the concentration

profiles obtained with the Boltzmann distribution (stagnant liquid conditions). Due to the total rejection of the solutes by the semi-permeable membrane, the concentration values obtained for the permeable system are much higher than those given by Boltzmann distribution.

A maximum is observed in the Cl^- concentration (Figure 7.6b). Near the membrane, the solvent is depleted of Cl^- because this ion is repelled by the membrane. Nevertheless, Cl^- accumulates in the boundary layer due to the convective transport. The maximum results from the balance between this transport and the electrical repulsion by the membrane.

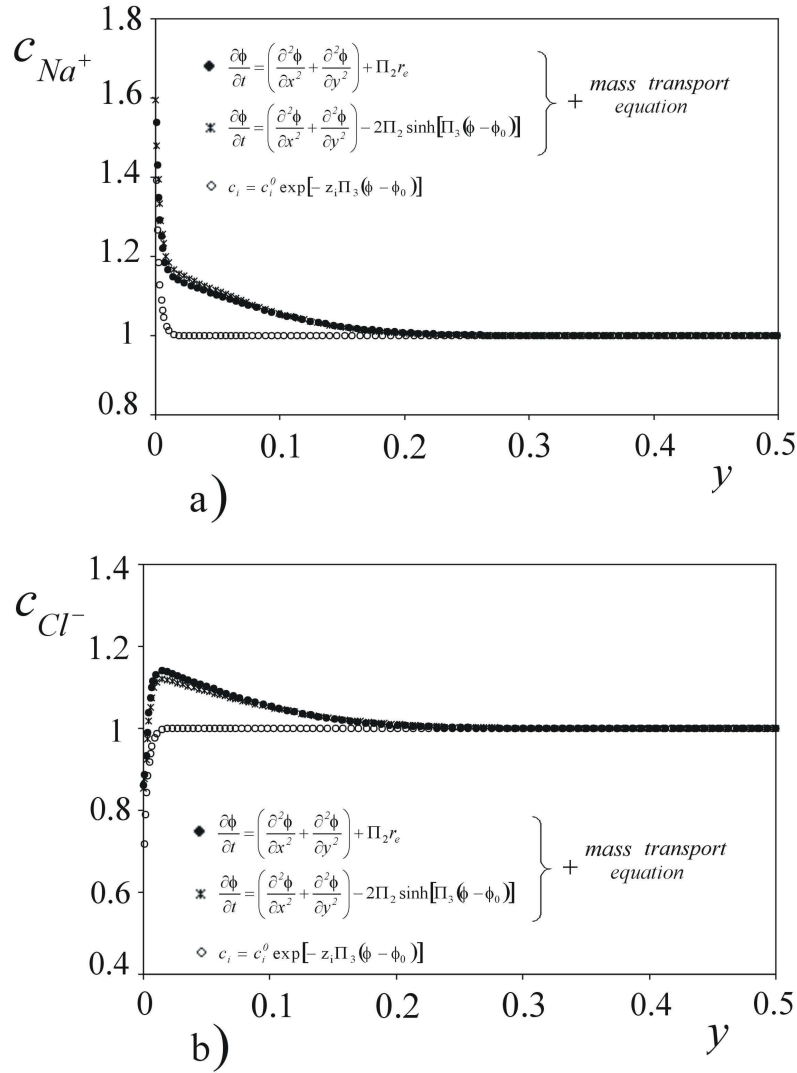


Figure 7.6 – a) Normalized concentration of Na^+ ; b) Normalized concentration of Cl^- , along the vertical direction, y , at the end of the negatively charged semi-permeable membrane, $x = 260$

$$(C_{\text{Na}^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3, C_{\text{Cl}^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3, \text{Re} = 100, \text{Pe}_{\text{Na}^+} = 7.14 \times 10^4,$$

$$\text{Pe}_{\text{Cl}^-} = 4.68 \times 10^4, \Pi_1 = 1.07 \times 10^{-4}, \Pi_2 = 1.36 \times 10^5, \Pi_3 = 0.387, \Delta P_0 = 1 \times 10^4 \text{ Pa}).$$

The concentration profiles in Figure 7.6 depend on the Peclet number (Figure 7.7). For decreasing Peclet numbers, the concentration profiles converge to those given by Boltzmann distribution. For small Peclet numbers, the tangential convection is negligible and the mass transport becomes similar to the mass transport in a stagnant liquid, for which the Boltzmann distribution is accurate.

The electric potential as a function of the normal distance to the membrane is represented in Figure 7.8. This figure shows that the electric potential obtained by solving the coupled Poisson-Boltzmann and Nernst-Planck equations is higher than that obtained by solving the Poisson-Boltzmann equation assuming Boltzmann distribution (Pinto et al. [1]). The difference results from the fact that the ionic concentrations are also significantly different. The electric potential has a maximum in a region very close to the membrane surface.

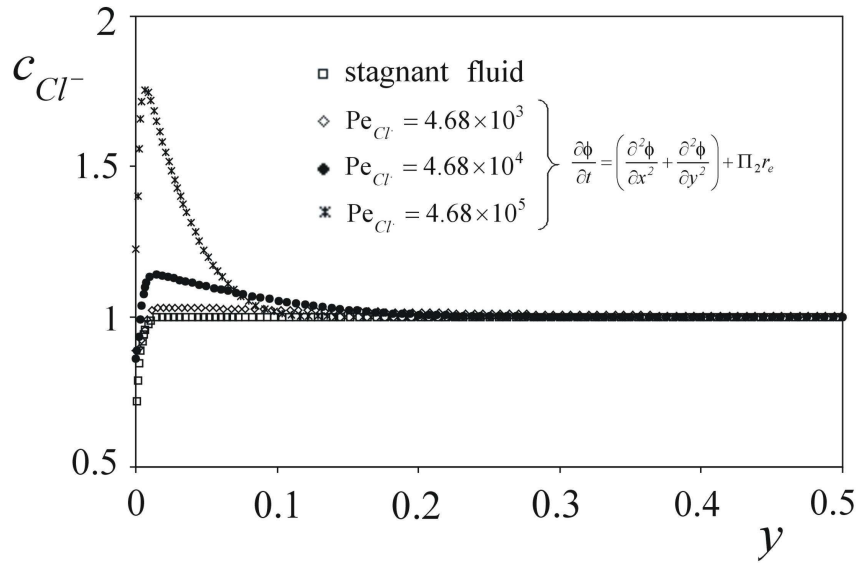


Figure 7.7 – Normalized concentration of Cl^- along the vertical direction, y , at the end of the negatively charged semi-permeable membrane ($x = 260$), for different Pe_{Cl^-} number: $\text{Pe}_{\text{Cl}^-} = 4.68 \times 10^3$, $\text{Pe}_{\text{Cl}^-} = 4.68 \times 10^4$ and $\text{Pe}_{\text{Cl}^-} = 4.68 \times 10^5$ ($C_{\text{Cl}^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $\text{Re} = 100$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^{-5}$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

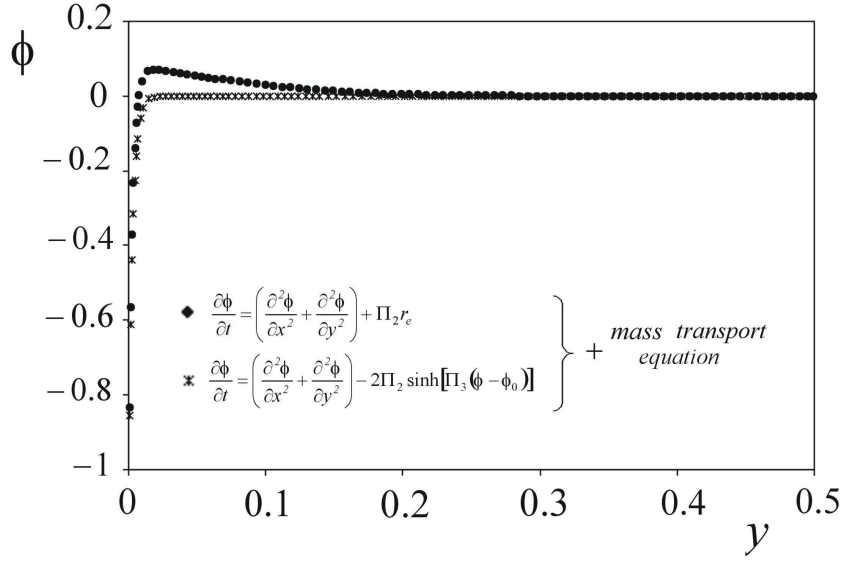


Figure 7.8 – Non-dimensional electric potential along the vertical direction, y , at the end of the negatively charged semi-permeable membrane, $x = 260$ ($C_{Na^+}^0 = 2.30 \times 10^{-8}$ kg/m³, $C_{Cl^-}^0 = 3.545 \times 10^{-8}$ kg/m³, $Re = 100$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4$ Pa).

7.5.2. Coupling electric and flow fields

The separation of two macromolecules, M_1 and M_2 , in an ionic solution of NaCl, was used to study the effect of the electric term of the vorticity equation. A conventional cell with only one negatively charged semi-permeable membrane was simulated. The results are represented in Figure 7.9.

Figure 7.9 shows that the velocity profiles (Figures 7.9a and 7.9b), obtained by solving the vorticity equation with and without the electric term, are similar. As a consequence, the concentration profiles and the electric field are also unaffected by the electric term (Figures 7.9c, 7.9d and 7.9e).

Figure 7.9d shows that the concentration fields interact with the potential field leading to the formation of a maximum of the electric field for $y=0.005$. This maximum attracts the negatively charged ions and repels the positively charged ions. In the case of species with high diffusivity, a pronounced maximum (Cl^-) and a pronounced minimum (Na^+) are observed.

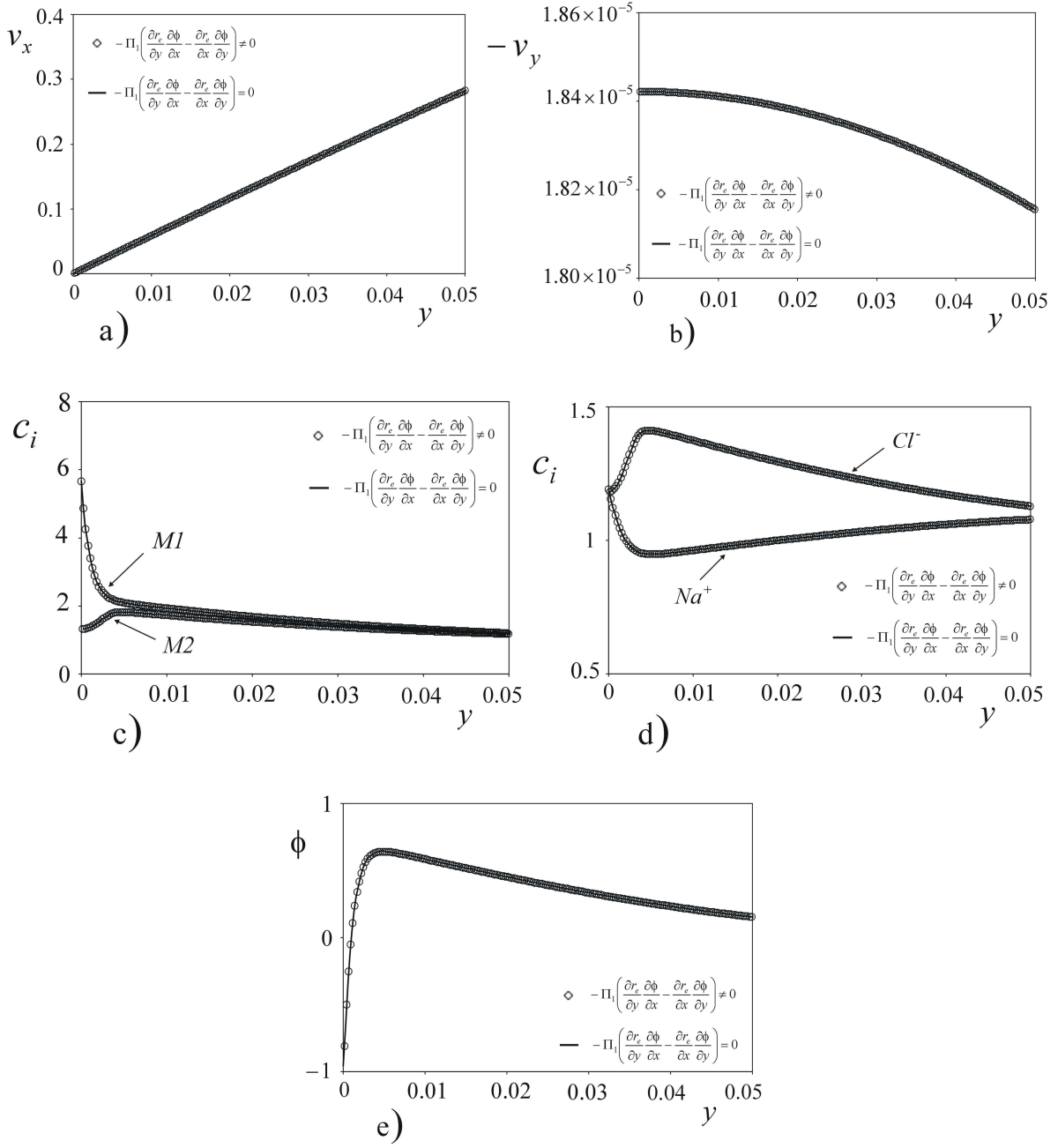


Figure 7.9 – a) Longitudinal velocity component; b) Normal velocity component, c) Normalized concentration of M_1 and M_2 ; d) Normalized concentration of Na^+ and Cl^- ; e) Non-dimensional electric potential, at the end of the negatively charged semi-permeable membrane, $x = 260$ ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $Re = 100$, $Pe_{M1} = 1.30 \times 10^6$, $Pe_{M2} = 8.00 \times 10^4$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

7.5.3. Fractionation of two macromolecules in a HMC

The fractionation of two macromolecules, M_1 and M_2 , in a HMC was numerically simulated. Figure 7.10 compares the concentration of the solutes at the membrane surface for a system with electrically charged semi-permeable membranes ($\Phi_w^s = -0.01$) with data from a system with electrically neutral semi-permeable membranes ($\Phi_w^s = 0$). Figure 7.11 is a detailed representation of the concentration profiles at the surface of the second fully-permeable membrane.

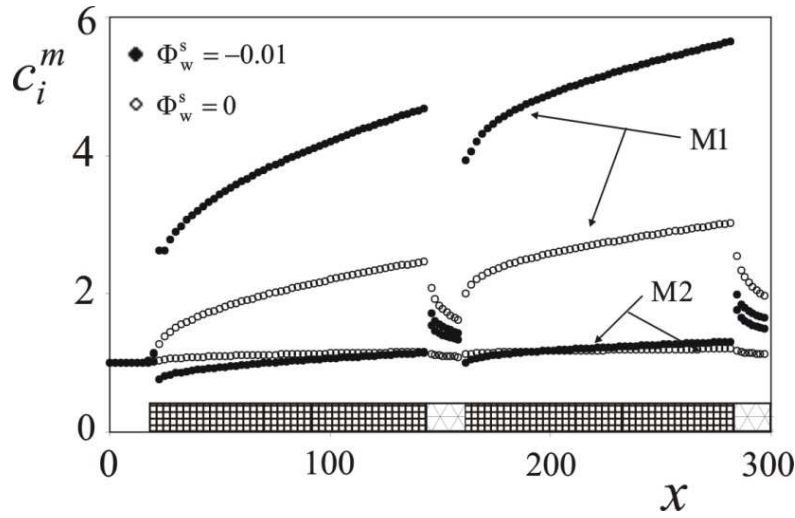


Figure 7.10 – Normalized concentration profiles of M_1 and M_2 along the tangential direction, x , at the hybrid membrane cell surface ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $Re = 100$, $Pe_{M1} = 1.30 \times 10^6$, $Pe_{M2} = 8.00 \times 10^4$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

When negatively charged semi-permeable membranes are used:

- the concentration of the positively charged macromolecule (M_1) is higher at the semi-permeable membrane surface and lower at the fully-permeable membrane surface;
- the concentration of the negatively charged macromolecule (M_2) is lower at the surface of the semi-permeable membranes and higher at the surface of the fully-permeable membranes.

At the surface of the semi-permeable membrane, the separation of the components increases because the electrical effects add to the diffusional effects. The component with the lower diffusivity is also the positively charged component and so its concentration over the surface of the semi-permeable membrane increases. The opposite occurs with the negatively charged component: higher diffusivity and electrical repulsion contribute to a low concentration of this component over the semi-permeable membrane.

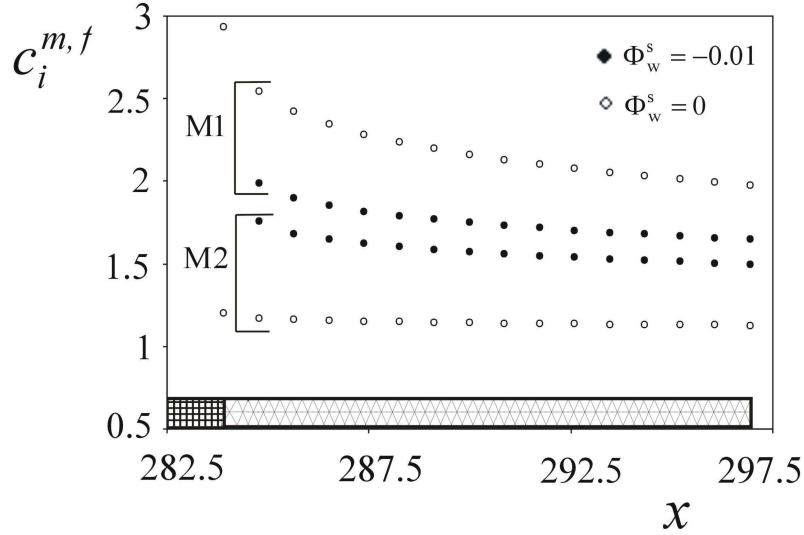


Figure 7.11 – Normalized concentration profiles of M_1 and M_2 along the last (2nd) fully-permeable sub-section at the hybrid membrane cell surface ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $Re = 100$, $Pe_{M1} = 1.30 \times 10^6$, $Pe_{M2} = 8.00 \times 10^4$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

At the surface of the fully-permeable membranes, the separation of the components decreases. To understand this decrease, the concentration field in the region near the surface of the membranes must be analysed. The concentration fields of the positively charged component in this region are represented in Figure 7.12 for $\Phi_w^s = -0.01$ and $\Phi_w^s = 0$.

The concentration at the fully-permeable membranes is a consequence of the transport of solutes along the streamlines that cross these sub-sections. The concentration of the positively charged component along these streamlines, in the region slightly above the end of

the semi-permeable membranes, is lower for $\Phi_w^s = -0.01$. The reverse phenomenon occurs for the negatively charged component.

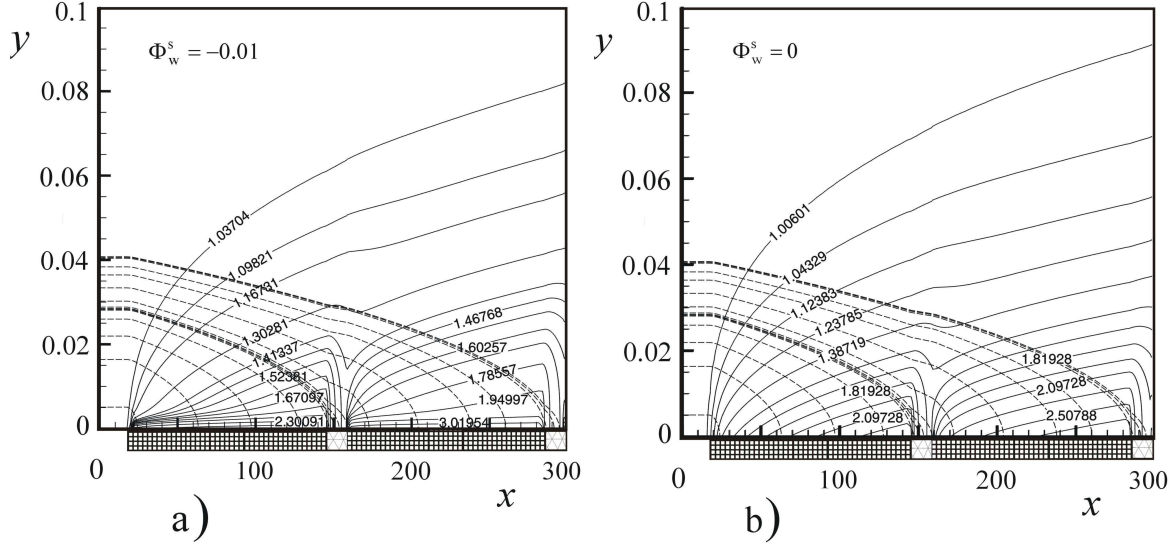


Figure 7.12 – Streamlines and iso-concentration lines of M_1 : a) negatively charged semi-permeable membrane, $\Phi_w^s = -0.01$; b) neutral semi-permeable membrane, $\Phi_w^s = 0$ ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $Re = 100$, $Pe_{M1} = 1.30 \times 10^6$, $Pe_{M2} = 8.00 \times 10^4$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

Figure 7.13 shows the concentration profiles along the vertical direction, y , at the end of the second semi-permeable membrane. In the region crossed by the streamlines of the concentrate stream (around $y = 0.005$), the concentration of M_1 is lower for $\Phi_w^s = -0.01$ than for $\Phi_w^s = 0$ and the concentration of M_2 is higher for $\Phi_w^s = -0.01$ than for $\Phi_w^s = 0$. For $y = 0.005$, the concentration of M_1 has a sudden change in slope and the concentration of M_2 has a maximum. These features of the concentration profiles are related to a maximum in the electric potential (Figure 7.14). This maximum, $\phi = 0.6$, repels the positively charged component and attracts the negatively charged one.

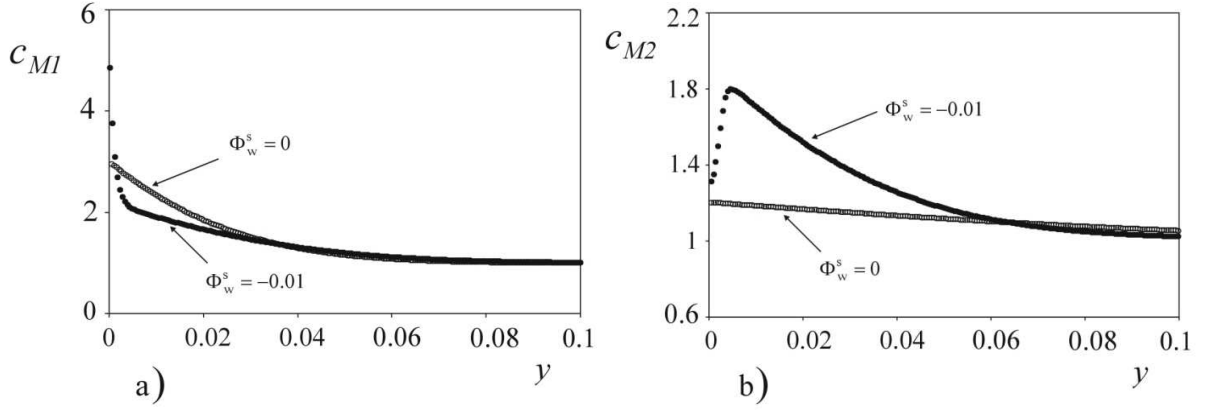


Figure 7.13 – a) Normalized concentration profile of M_1 ; b) Normalized concentration profile of M_2 along the vertical direction, y , at the end of the last (2nd) negatively charged semi-permeable membrane, $x = 260$ ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $\text{Re} = 100$, $\text{Pe}_{M1} = 1.30 \times 10^6$, $\text{Pe}_{M2} = 8.00 \times 10^4$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

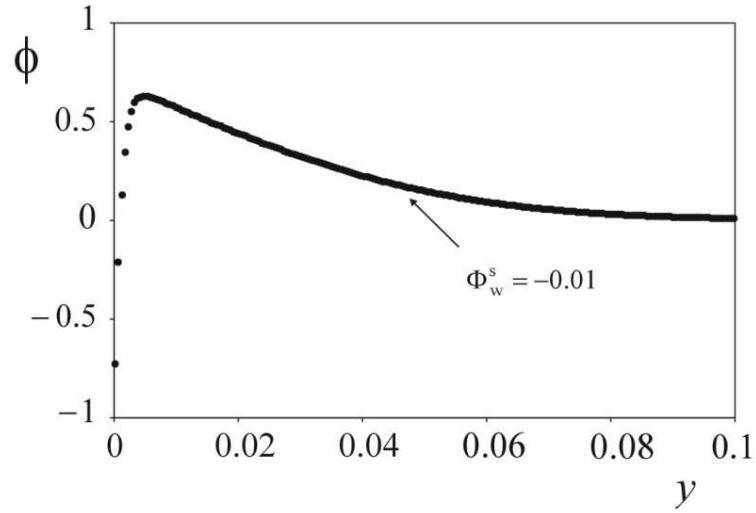


Figure 7.14 – Non-dimensional electric potential along the vertical direction, y , at the end of the last (2nd) negatively charged semi-permeable membrane, $x = 260$ ($C_{M1}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{M2}^0 = 1.00 \times 10^{-5} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $\text{Re} = 100$, $\text{Pe}_{M1} = 1.30 \times 10^6$, $\text{Pe}_{M2} = 8.00 \times 10^4$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

7.6. Conclusions

A new numerical code was developed to simulate the fractionation of macromolecules by membrane cells. The main goal is to extend to multi-component ionic solutions the code developed by Pinto et al. [1] for binary ionic solutions.

The Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations were solved by numerical methods, without any simplification. The results were compared with those given by a simplified version developed by Pinto et al. [1]. The data from both methods, for a binary ionic solution, are very similar. If the Peclet number of the components is low (high diffusivity), the convection is negligible relatively to the diffusion. In this case, the solution is similar to that obtained considering stagnant fluid.

A sensitivity analysis of the electric terms of the vorticity equation was also done. The influence of the electric terms of the vorticity equation on the numerical results is negligible.

The new numerical code was applied to the fractionation of two macromolecules using a hybrid membrane cell (HMC). The HMC comprised neutral fully permeable membranes and semi-permeable membranes with the charge of the component with higher diffusivity. The numerical results were compared to those in a HMC but supposing semi-permeable membranes electrically neutral. The separation improves in the boundary layer over the semi-permeable membrane. However, the separation in the fully-permeable membranes is lower.

In a future work, the numerical code developed will be applied to the separation of two macromolecules by a hybrid membrane cell but with charged semi-permeable membranes selective to the components, i. e., permeable to the macromolecules, according to the size of macromolecules and to the membrane pore size. In this type of cell, it is expected that electric effects can increase the separation, as long as the most transmitted component through the membrane is also the most electrically attracted to the membrane.

7.7. Nomenclature

C_i	Concentration of component i
c_i	Normalized concentration of component i
C_i^0	Concentration of component i at the feed/bulk
c_i^0	Normalized concentration of component i at the feed/bulk
C_{ref}^0	Concentration of the reference component at the feed/bulk
c_{ref}^0	Normalized concentration of the reference component at the feed/bulk
$C_{M,i}^0$	Molar concentration of component i at the feed/bulk
$c_{M,i}^0$	Normalized molar concentration of component i at the feed/bulk
C_i^m	Concentration of component i at membrane surface
c_i^m	Normalized concentration of component i at membrane surface
$C_i^{m,f}$	Concentration of component i at fully-permeable membrane surface
$c_i^{m,f}$	Normalized concentration of component i at fully-permeable membrane surface
$C_{i,crit}^k$	Concentration of component i on a critical location
$c_{i,crit}^k$	Normalized concentration of component i on a critical location
$\overline{C}_i^{m,s}$	Mean concentration of component i at semi-permeable membrane surface
$\overline{c}_i^{m,s}$	Mean normalized concentration of component i at semi-permeable membrane surface
$\overline{C}_i^{m,s,refgrid}$	Mean concentration of component i at semi-permeable membrane surface for a reference grid
$\overline{c}_i^{m,s,refgrid}$	Mean normalized concentration of component i at semi-permeable membrane surface for a reference grid
D_i	Molecular diffusivity of component i
F	Faraday constant
H	Distance between parallel plates
k	Current time step
L_{out}	Length of the outlet section

L_{in}	Length of the inlet section
L_m	Total length of the membrane
L_s^-	Length of the negatively charged semi-permeable sub-section
$\sum_{k=1}^n L_{s,k}^-$	Total length of the negatively charged semi-permeable membrane
L_f	Length of the neutral fully-permeable sub-section
$\sum_{k=1}^n L_{f,k}$	Total length of the neutral fully-permeable membrane
L	Total length of the cell
M_i	Molar mass of component i
M_{ref}	Molar mass of the reference component
m	Total number of nodes in the vertical direction of the grid
n	Total number of nodes in the horizontal direction of the grid
ni_m	Number of nodes along the total length of the membrane
n_{sec}	Number of sections of the hybrid membrane cell
R	Gas constant
r_e	Sum of the normalized ionic concentrations
R_m	Membrane resistance of the semi-permeable membrane
T	Temperature
t	Non-dimensional time
V_0	Mean feed velocity
V_x	Longitudinal component of the velocity
v_x	Normalized longitudinal component of the velocity
$\hat{v}_x$	Normalized pseudo-velocity (component x)
V_y	Vertical component of the velocity
v_y	Normalized vertical component of the velocity
$\hat{v}_y$	Normalized pseudo-velocity (component y)
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Y	Vertical coordinate
y	Normalized vertical coordinate

z_i Electric charge of component i

Non-dimensional numbers

Pe_i Peclet number of component i
 Re Reynolds number of the solution
 Π_1 Non-dimensional number defined by equation 7.13
 Π_2 Non-dimensional number defined by equation 7.2
 Π_3 Non-dimensional number defined by equation 7.21

Greek Symbols

ΔP_0 Static pressure difference across the semi-permeable membrane
 Δt Time step range
 ε Permittivity
 $\varepsilon_{ci_{crit}}$ Numerical error of the concentration of component i on a critical location
 $\varepsilon_{\phi_{crit}}$ Numerical error of the electric potential on a critical location
 $\varepsilon_{\omega_{crit}}$ Numerical error of the vorticity on a critical location
 $\varepsilon_{c_i}^{-m,s}$ Discretization error of concentration of component i at semi-permeable
membrane surface
 ψ Stream function
 ω Vorticity
 ω_{crit}^k Vorticity on a critical location
 ρ Density
 $\bar{\mu}$ Mean viscosity of the solution
 Φ Electric potential
 ϕ Normalized electric potential
 Φ_0 Electric potential of the bulk
 ϕ_0 Normalized electric potential of the bulk
 Φ_w Membrane electric potential
 ϕ_w Normalized membrane electric potential

Φ_w^s	Electric potential at semi-permeable membrane surface
ϕ_{crit}^k	Normalized electric potential on a critical location

7.8. References

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Application of the stagnant film equation to electrophoretic migration of proteins near ultrafiltration membranes – comparison with CFD results

In membrane separation processes, the film equation is frequently used to predict the permeate velocity. In the present work, the applicability of the film equation, based on a convective-diffusive-electrophoretic migration (CDE) model, is evaluated using numerical data. CDE model accounts for the transport of charged solutes in the boundary layer over a charged membrane. Two versions of the film equations, based on two different models, were developed: in one of the models, the membrane induces a non-linear electric field, in the other, the electric field is uniform. To evaluate the accuracy of the film equations and their range of validity, an in house code was developed which solves the Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations.

The Sherwood numbers, along the membrane length, of BSA (Bovine Serum Albumin) and LYS (Lysosyme) of an ionic solution of NaCl were determined by the film equations. The permeate velocities, solute concentrations and rejection coefficients obtained by the numerical code were used as input to the film equations. For values of the non-dimensional number $|z_i \times F\Phi_w / (RT)|$ lower than 0.284, the Sherwood number along the membrane, determined by the film equation for a non-linear electric field, is independent of the electric potential at the membrane surface. For values of the non-dimensional number $|z_i \times E_f H / \Phi_w|$ between 0.03 and 420, the Sherwood profiles, determined by the film equation for a constant electric field, are also independent of the electric field. In these ranges, Sherwood number profiles are identical to those in an impermeable cell, and so, the impermeable profiles can be used to make predictions based on the film equations. Film equation for a constant electric field was used to predict the apparent selectivity of the separation of BSA and LYS in an ionic solution of NaCl and the mean deviation is 6%.

The contents of this chapter were adapted from: S.I.S. Pinto, J.M. Miranda, J.B.L.M. Campos, Application of the stagnant film equation to electrophoretic migration of proteins near ultrafiltration membranes – comparison with CFD results, submitted for publication in the journal *Chemical Engineering Science* (2011).

8.1. Introduction

Protein separation by ultrafiltration has been intensively applied in such diverse fields as food industry and biotechnology. Several types of techniques have been explored to increase the efficiency of the separation [1-14]. However, in most numerical studies [9-14] the electric interactions between proteins and electric charged membranes have been neglected.

Separation techniques such as protein fractionation by differential diffusion [11] or protein fractionation by a selective membrane [9, 12] have been explored by the authors of this work. Interactions between different proteins and interactions between membrane and proteins were disregarded in those numerical studies. These assumptions are accurate if the components are at their iso-electric point and the membrane is not electrically charged.

In most practical situations, electric interactions are important and can not be neglected. Numerical [15, 16] and analytical [17-20] methods have been developed to deal with electrical effects on the vicinity of a charged membrane. Numerical studies about mass transport in the vicinity of a charged membrane are based on the solution of the Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations. The numerical methods implemented allow the determination of the flow, concentration and electric fields. Pinto et al. used this approach to study the variation of the electric field, in a bidimensional cell, with the ionic concentrations of the components [15, 16].

Analytical methods are based on the stagnant film model. An equation relating the permeate velocity with the electric field is derived from a mass balance to a stagnant film located in the vicinity of the membrane. Sarkar et al. [17] used the film model to establish the gel layer resistance in their study about fractionation of bovine serum albumin (BSA) and lysosyme (LYS) for several values of pH (7.4; 8.6; 11). The proteins have distinguished and opposite electric charges and the fractionation occurs under a constant external electric field. Rabiller-Baudry et al. [18] studied the application of a convective-diffusive-electrophoretic (CDE) migration model to the ultrafiltration of LYS. The CDE model developed accounts for the transfer of a charged solute (LYS) in the boundary layer of an ultrafiltration membrane. The authors assumed total rejection of LYS by the membrane. The study was done for different pH values and different ionic strengths of the solute. The model developed was used to determine the concentration of the solute at the membrane surface, as well as the

solute concentration profiles in the polarized layer. Experimental data of the zeta-potential of the membrane, experimental electrophoretic mobility of the solute and convective and diffusive transport data of the solute were the inputs of the model. Rabiller-Baudry et al. [16] compared the results obtained with the CDE model with data from a convective-diffusive model (CD). The concentration profiles along the boundary layer taken with the CDE model show a maximum in a very small distance to the membrane. This maximum is not predicted by the CD model [16]. Vasan et al. [19, 20] also developed a model to determine the concentration profile of a charged solute in a polarized layer. The results showed an excellent agreement with the numerical/experimental data reported by Rabiller-Baudry et al. [18].

The stagnant film model is a crude approximation of the flow field in the vicinity of the membrane. The resulting film equation has, therefore, limitations. Miranda and Campos [21] studied the accuracy of the stagnant film model when applied to a convective-diffusive separation (CD model), where the electrophoretic mobility of the solute was disregarded. The authors compared the Sherwood number of an impermeable cell (considering uniform mass production or uniform concentration at the wall), with the Sherwood number of a permeable cell predicted by the film equation using, as input, the surface concentrations and the permeate velocities obtained numerically in a house developed code. They concluded that the film equation (using Sherwood number of an impermeable cell) is accurate for low and moderate Peclet numbers and permeate velocities. As far as we know, the accuracy of the stagnant film equation obtained from a convective-diffusive-electrophoretic model is a topic not yet explored in the literature.

The authors have been developing a numerical code [15, 16] to study the separation of components taking into account electric interactions. They studied the separation of the ionic components of a solution of NaCl assuming that the convective effect of the flow on the ionic distribution was negligible [15]. The electric potential was determined by a simplified method taking the Boltzmann distribution of the charged ions. In a second approach [16], the Poisson-Boltzmann, the Nernst-Planck and the Navier-Stokes equations were solved simultaneously without the above simplification. A numerical method was developed to deal with the coupling between electric and concentration fields of all species in solution. The complete description of concentration, velocity and electric fields was obtained in a bidimensional domain. In these studies, the authors considered total rejection of the

components by the membrane. However, in macromolecules fractionation, different components have different transmissions through the membrane pores [9, 12, 22, 23].

In the present study, numerical data are used to evaluate the accuracy of the film equation. Numerical simulations take on account the transmissions of the components through the membrane pores [22, 23]. The film equation is based on a CDE model. Two versions with different assumptions will be deduced: one for a non-linear electric field near the membrane and the other for a constant electric field.

Afterwards, the film equation, considering a constant electric field, will be applied to predict the apparent selectivity of the fractionation of a solution of BSA and LYS. The accuracy of the prediction will be compared with numerical data. Membrane will be electrically charged and a diluted solution will be assumed in order to neglect solute-solute interactions [9]. The importance, to the apparent selectivity of the electric interactions membrane-solutes, will be analysed.

8.2. Cell description

The parallel plate cell under study comprises membranes with a negative zeta-potential value, Φ_w , which are permeable to the solvent and partially permeable to the solutes (Figure 8.1).

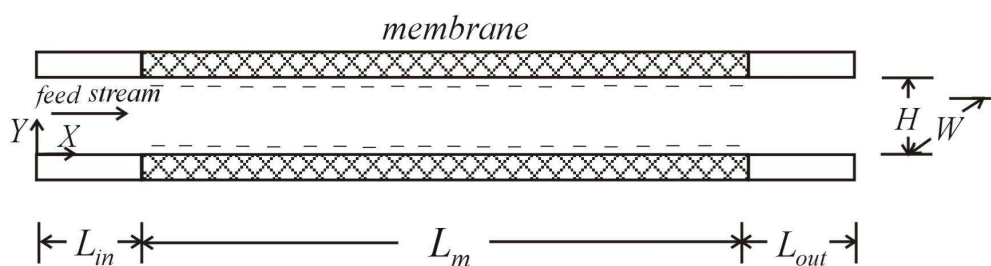


Figure 8.1 – Cell composed of negatively charged membranes.

In the separation process, the feed stream is separated into two streams: the retentate stream, which leaves the cell through the principal channel and the permeate stream that crosses the membrane. The feed stream is composed by a mixture of two proteins, bovine

serum albumin (BSA) and lysosyme (LYS), in an ionic solution of NaCl (Na^+ and Cl^-). The feed stream is electrically neutral.

The retentate stream and the permeate stream are composed by all the species. The separation is done according to the solutes-membrane electric interactions and also to the transmission of the solutes through the membrane.

The characteristics of the cell used are listed in Table 8.1 and the static pressure difference (ΔP_0) between the two sides of the membrane is 1×10^4 Pa.

Table 8.1 - Characteristics of the cell.

Membrane	OMEGA Polysulfone membrane 50 kDa MWCO
R_m	$5.714 \times 10^{12} \text{ m}^{-1}$
H	0.001 m
L_m	0.040 m
$L_{in} = L_{out}$	0.02 m

8.3. General assumptions and physical properties

In the present numerical study some general assumptions were adopted:

- The pH of the buffer solution is constant and equal to 7.4;
- The semi-permeable membrane is selective to the components;
- The osmotic pressures of the proteins, BSA and LYS, and of the ionic species, Na^+ and Cl^- , are considered negligible, since the concentrations of these species are, everywhere in the cell, including over the semi-permeable membranes, very low (dilute solution);
- The transport properties (viscosity and diffusivity) of all the species are considered constant. In a very diluted solution, viscosity and diffusivity are practically independent of the concentration of the species, including at the membrane surface;
- The viscosity of the solution is considered identical to that of pure water everywhere inside the cell (very diluted solution);
- Electric effects inside the membrane pores are not considered;

- The proteins are assumed to be non-interacting. Diluted feed solution and low feed velocity were used to make this assumption accurate [9].

The properties of the components are given in Table 8.2.

Table 8.2 – Properties of the components BSA and LYS in an ionic solution of NaCl.

Component	BSA ^[a]	LYS ^[a]	Na ⁺ ^[a]	Cl ⁻ ^[a]
M_i (kg/kmol)	69000	14600	23	35.45
z_i	-21 ^[b]	+3 ^[c]	+1	-1
D_i (m ² /s)	7.0×10^{-11} ^[d]	11.8×10^{-11} ^[d]	1.33×10^{-9} ^[e]	2.03×10^{-9} ^[e]
C_i^0 (kg/m ³)	6.90×10^{-5}	1.02×10^{-4}	2.30×10^{-8}	3.545×10^{-8}
$C_{M,i}^0$ (kmol/m ³)	1.0×10^{-3}	7.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}

^[a] solutes are the same used by Sarkar et al.[17]

^[b] Electric charge of BSA was taken from Chun et al. [24]

^[c] Electric charge of LYS was determined through its zeta-potential value - $\zeta_{LYS} = 6.7$ mV – Sarkar et al. [17]

^[d] diffusivities of BSA and LYS were taken from Sarkar et al. [17]

^[e] diffusivities of Na⁺ and Cl⁻ were taken from Pivonka et al. [25]

8.4. Theory

8.4.1. Transmission model and selectivity

The apparent selectivity of a membrane (σ_{ap}) is defined by:

$$\sigma_{ap} = \frac{S_{ap_i}}{S_{ap_j}} = \frac{C_i^p / C_i^0}{C_j^p / C_j^0} \quad (8.1)$$

where S_{ap_i} and S_{ap_j} represent the apparent sieving coefficients, defined by the ratio between the concentration of a solute in the permeate, C_i^p or C_j^p , and the concentration of the solute

in the bulk, C_i^0 or C_j^0 . The subscript i indicates the preferentially transmitted solute (LYS) and j the preferentially rejected solute (BSA).

The transmission of the solutes was described by a convective-diffusive transport model (Opong and Zydney [23]):

$$S_i = \frac{S_{i,\infty} \exp\left[(S_{i,\infty} V_m \delta_m) / D_{i,eff}\right]}{S_{i,\infty} + \exp\left[(S_{i,\infty} V_m \delta_m) / D_{i,eff}\right] - 1} \quad (8.2)$$

where $S_{i,\infty}$ is the asymptotic intrinsic sieving coefficient of component i , δ_m the membrane thickness and $D_{i,eff}$ the effective diffusivity of component i along the membrane pore. The asymptotic intrinsic sieving coefficient depends on the ratio between the equivalent molecular radius of the component (r_i^*) and the specific area of the pores (s).

The equivalent molecular radius of proteins BSA and LYS are listed in Table 8.3. The equivalent molecular radius of BSA was determined from data of Tencer et al. [26] and the equivalent molecular radius of LYS was taken from Sarkar et al. [17]. The specific area of the pores (s) of the OMEGA Polysulfone Membrane 50 kDa MWCO was obtained based on experimental data of Opong and Zydney [23] and is equal to 1.86 nm.

Table 8.3 - Values of equivalent molecular radius (r_i^*) for BSA and LYS.

Component	r_i^* (nm)
BSA	3.04
LYS	2.09

The rejection coefficient of a component is related to the transmission by:

$$R_i = 1 - S_i \quad (8.3)$$

and it is dependent on the velocity, V_m , in each point at the membrane surface, equation (8.2). More details about the procedure are described in Pinto et al. [12].

8.4.2. Numerical method

Electric, concentration and flow fields were determined to study the effect of the electric interactions between membrane and components in the separation of the proteins. The Poisson-Boltzmann, the Nernst-Planck and the Navier-Stokes equations were solved by numerical methods (CFD).

8.4.2.1. Conservative equations

The equations were solved in the numerical domain represented in Figure 8.2. Grid for simulations was selected after performing several grid tests according to the procedure described by Pinto et al. [15, 16]. The grid selected for the numerical domain is composed by 117×501 nodes.

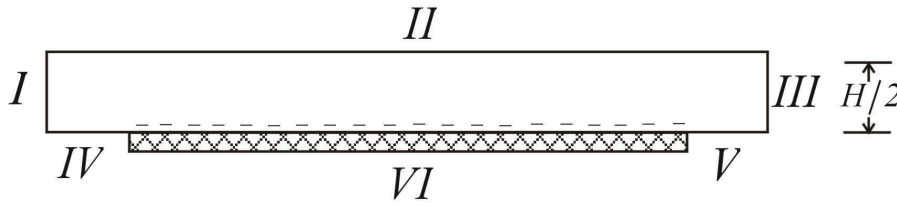


Figure 8.2 – Schematic representation of the domain of a cell with a permeable membrane and respective boundaries (I – cell inlet; II – symmetric axis; III – cell outlet; IV – impermeable wall; V – impermeable wall ; VI – membrane with negative zeta-potential).

For a better understanding of the conservative equations, the uppercase variables will symbolize dimensional variables and the lowercase normalized variables. The electric potential is normalized by the absolute value of the membrane potential (Φ_w), concentrations by the inlet concentrations of the solutes (C_i^0), velocities by the inlet velocity (V_0) and geometric dimensions by the height of the cell (H).

Assuming point charges, the electric potential follows the Poisson-Boltzmann equation:

$$\frac{\partial \phi}{\partial t} = \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right) + \Pi_2 r_e \quad (8.4)$$

where ϕ is the non-dimensional electric potential, r_e the sum of the ionic concentrations of all the components and Π_2 a non-dimensional number defined by:

$$\Pi_2 = \frac{FC_{ref}^0 H^2}{\varepsilon M_{ref} \Phi_w} \quad (8.5)$$

where F is the Faraday constant, C_{ref}^0 the concentration of the reference component in the bulk, M_{ref} the molar mass of the reference component and ε the permittivity. The cation, Na^+ , was arbitrarily chosen as the reference component.

The sum of the normalized ionic concentrations was determined according to the local ionic concentrations:

$$r_e = \sum_{i=1}^N z_i \frac{C_i^0}{C_{ref}^0} \frac{M_{ref}}{M_i} c_i \quad (8.6)$$

where z_i is the electric charge of component i , c_i the normalized concentration of component i and M_i the molar mass of component i . The index *ref* refers to the reference component.

The flow in the cell is described by the Navier-Stokes equations. For a bi-dimensional cell, the Navier-Stokes equations can be written for secondary variables (vorticity, ω , and stream function, ψ) as the vorticity transport equation and a Poisson type equation.

In Cartesian coordinates (x and y), the vorticity transport equation is given by:

$$\frac{\partial \omega}{\partial t} + v_x \frac{\partial \omega}{\partial x} + v_y \frac{\partial \omega}{\partial y} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) - \Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) \quad (8.7)$$

where Π_1 is a non - dimensional number defined by:

$$\Pi_1 = \frac{FC_{ref}^0 \Phi_w}{M_{ref} \rho V_0^2} \quad (8.8)$$

where ρ is the fluid density and V_0 the feed velocity.

The Reynolds number (Re) is given by:

$$\text{Re} = \frac{\rho V_0 H}{\mu} \quad (8.9)$$

where $\bar{\mu}$ is the mean viscosity of the solution.

The Poisson Equation for the stream function is:

$$\omega = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \quad (8.10)$$

and the velocity components are related to the stream function by:

$$v_x = \frac{\partial \psi}{\partial y}; \quad v_y = -\frac{\partial \psi}{\partial x} \quad (8.11)$$

The Nernst-Planck equation of each component i is given by:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(\hat{v}_{xi} c_i)}{\partial x} + \frac{\partial(\hat{v}_{yi} c_i)}{\partial y} = \frac{1}{\text{Pe}_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (8.12)$$

where

$$\hat{v}_{xi} = \left(v_x - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial x} \right) \quad (8.13)$$

$$\hat{v}_{yi} = \left(v_y - \frac{z_i \Pi_3}{\text{Pe}_i} \frac{\partial \phi}{\partial y} \right) \quad (8.14)$$

The components of the pseudo-velocity, $\hat{v}_{xi}$ and $\hat{v}_{yi}$, are specific of each component i , since they depend on the respective Peclet number.

The mass transport equation was divided into two simpler conservative equations and solved, sequentially, through the fractional-step-method with the pseudo-convective terms separated from the diffusive terms:

$$\frac{\partial c_i}{\partial t} + \frac{\partial(\hat{v}_{xi}c_i)}{\partial x} + \frac{\partial(\hat{v}_{yi}c_i)}{\partial y} = 0 \quad (8.15)$$

$$\frac{\partial c_i}{\partial t} = \frac{1}{Pe_i} \left(\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} \right) \quad (8.16)$$

Peclet number of component i (Pe_i) is based on its diffusivity (D_i):

$$Pe_i = \frac{V_0 H}{D_i} \quad (8.17)$$

and Π_3 is a non-dimensional number defined by:

$$\Pi_3 = \frac{F\Phi_w}{RT} \quad (8.18)$$

More details about the discretization, iterative method and conditions for boundaries I, II, III, IV and V (Figure 8.2) are described by Pinto et al. [15, 16]. In these studies, the membrane totally rejects the solutes, and so the boundary conditions for the membrane surface can not be applied to the present work. This will be presented in the following section.

8.4.2.2. Boundary condition of mass transport equation at membrane surface

The mass boundary condition at the membrane surface, boundary VI, was established by performing a mass balance to a volume of fluid contiguous to the membrane surface. The volume of fluid and respective pseudo-velocities along the normal direction, incoming $\hat{v}_{y_{up}}^m$, and, outgoing, $\hat{v}_{y_{down}}^m$, are represented in Figure 8.3.

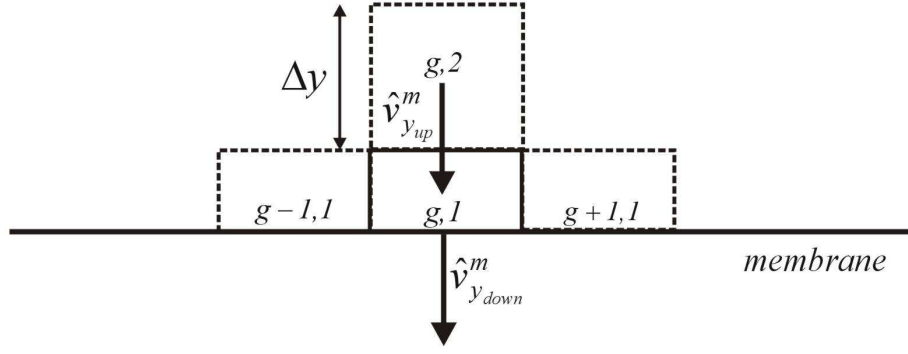


Figure 8.3 – Discretization detail at the membrane surface.

According to the finite volume method, the outcome of a mass balance to the control volume of Figure 8.3 is:

$$\frac{c_{g,1}^{k+1} - c_{g,1}^k}{\Delta t} = - \left(\frac{\hat{v}_{yu}^m c_{g,2}^{k+1} - \hat{v}_{yd}^m c_{g,1}^{k+1}}{\Delta y} \right) \quad (8.19)$$

where Δt is the time step, Δy the height of the node and the subscripts $(g,1)$ and $(g,2)$ refer to the node identification according to Figure 8.3.

The normalized concentration (c) of a component in a node over the membrane surface was obtained through an implicit method:

$$\left(\Delta t \frac{\hat{v}_{yd}^m}{\Delta y} - 1 \right) c_{g,1}^{k+1} - \Delta t \frac{\hat{v}_{yu}^m}{\Delta y} c_{g,2}^{k+1} = -c_{g,1}^k \quad (8.20)$$

The incoming pseudo-velocity to the node $(g,1)$, $\hat{v}_{yu}^m$ (Figure 8.3), is defined by the average between the pseudo-velocities at node $(g,1)$ and $(g,2)$:

$$\hat{v}_{yu}^m = \frac{\hat{v}_{y_{g,2}} + \hat{v}_{y_{g,1}}}{2} \quad (8.21)$$

The pseudo-velocity along the normal direction, leaving the discretized node $(g,1)$, $\hat{v}_{yd}^m$ (Figure 8.3), depends on the rejection coefficient ($R_{g,1}$) of the component and also on the pseudo-velocity at node $(g,1)$.

$$\hat{v}_{yd}^m = \hat{v}_{y,g,1} (1 - R_{g,1}) \quad (8.22)$$

Since the osmotic pressure is negligible (diluted solution), the permeate velocity through the membrane is (Lonsdale et al. [27]) given by:

$$-v_y = \frac{\Delta P_0}{\bar{\mu}_p R_m V_0} \quad (8.23)$$

where ΔP_0 is the applied pressure difference across the membrane, R_m the resistance of the membrane and $\bar{\mu}_p$ the viscosity of the permeate flux.

All the other conditions for boundary VI (Figure 8.2) have been presented by Pinto et al. [11, 15, 16]: boundary conditions for mass transport equation can be found in [15]; boundary conditions for flow equations in [11]; and boundary conditions for electric potential equation in [16].

8.4.2.3. Convergence

The convergence study of the numerical method was based on the following errors:

$$\mathcal{E}_{ci\,crit} = \left| \frac{C_{i,crit}^k - C_{i,crit}^{k-1}}{C_{i,crit}^k} \right| \quad (8.24)$$

$$\mathcal{E}_{\phi\,crit} = \left| \frac{\phi_{crit}^k - \phi_{crit}^{k-1}}{\phi_{crit}^k} \right|; \quad (8.25)$$

$$\mathcal{E}_{\omega_{crit}} = \left| \frac{\omega_{crit}^k - \omega_{crit}^{k-1}}{\omega_{crit}^k} \right| \quad (8.26)$$

where *crit* refers to the critical node and *k* to the current iteration. The variables are evaluated in a critical node located near the cell exit, where the convergence is slower. More details about the iterative process were already described by Pinto et al. [16].

To assure that the conservative equations converges to the correct solution, the total sum of the residues of the electric potential equation, R_ϕ , was determined by:

$$R_\phi = \sum_{g=2}^{n-1} \sum_{h=2}^{m-1} \left| \frac{\partial \phi}{\partial t} \right|_{g,h} \quad (8.27)$$

where $\left| \frac{\partial \phi}{\partial t} \right|_{g,h}$ is the time derivative of the electric potential at node (*g*, *h*).

An example of convergence, for the most severe conditions used (highest zeta-potential at membrane surface), is presented in Figure 8.4. The normalized concentrations, electric potential and vorticity converge to a constant value. The total residues of the electric potential equation, R_ϕ , decreases to a very small value. Based on the analysis of several simulations, the following criteria were adopted to stop the iterative process:

$$\left\{ \begin{array}{l} \mathcal{E}_{c_{i_{crit}}} < 10^{-3} \\ \mathcal{E}_{\phi_{crit}} < 10^{-3} \\ \mathcal{E}_{\omega_{crit}} < 10^{-3} \\ R_\phi < 10^{-2} \end{array} \right. \quad (8.28)$$

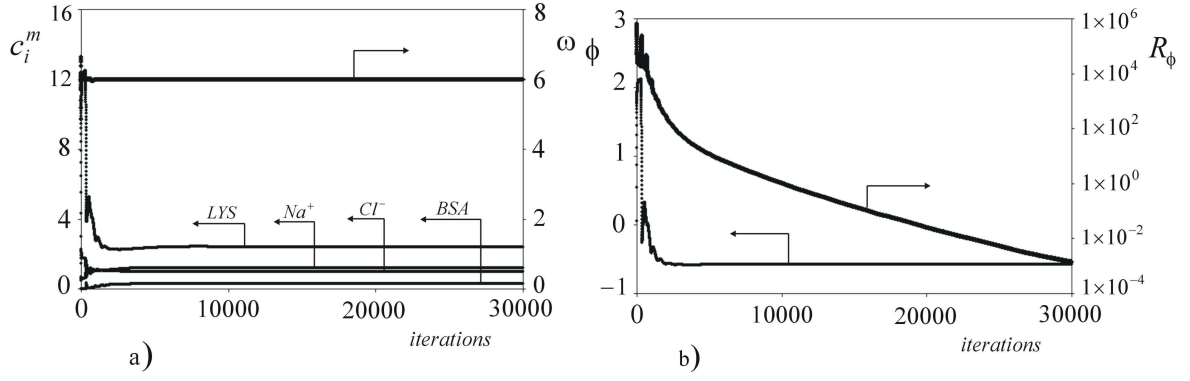


Figure 8.4 – a) Normalized concentration of the species and flow vorticity at the critical node versus the number of iterations; b) Normalized electric potential and total residues of the electric potential equation at the critical node versus the number of iterations ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $z_{BSA} = -21$; $z_{LYS} = +3$; $\Phi_w = -10\text{mV}$ ($|z_{BSA} \times \Pi_3| = 8.119$ and $|z_{LYS} \times \Pi_3| = 1.160$), $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

8.4.3. Film equation

Two versions of the film equation were developed, one for a non-linear electric potential along the normal direction to the membrane – film equation **I** – and another for a linear relation of the electric potential along the normal direction to the membrane – film equation **II**.

A mass balance (considering convection, diffusion, electrophoretic mobility and transmission through the membrane) to a stagnant film in the vicinity of the membrane surface is schematically represented in Figure 8.5.

The equation representing the mass balance is:

$$V_m C_i = -D_i \frac{\partial C_i}{\partial Y} - \mu_i C_i \frac{\partial \Phi}{\partial Y} + \mu_i C_i^p \frac{\partial \Phi}{\partial Y} \Big|_{Y=0} + V_m C_i^p \quad (8.29)$$

where V_m is the velocity at the membrane surface, D_i the diffusivity of component i , C_i the concentration of component i , C_i^p the concentration of component i in the permeate flux, Φ

the electric potential and μ_i the electrophoretic mobility of component i . The electrophoretic mobility is:

$$\mu_i = z_i \frac{FD_i}{RT} \quad (8.30)$$

where z_i is the electric charge of component i .

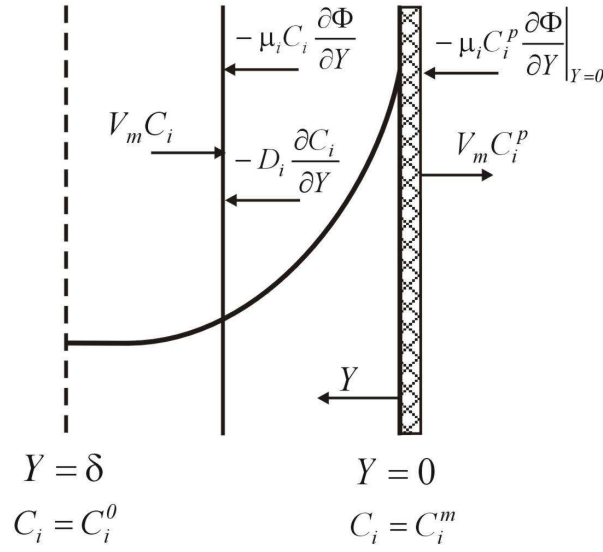


Figure 8.5 - Generic mass balance to the control volume in the boundary layer at the membrane surface.

8.4.3.1. Total rejection and non-linear electric potential (I)

Supposing total rejection, $C_i^p = 0$, the mass balance becomes:

$$V_m C_i = -D_i \frac{\partial C_i}{\partial Y} - \mu_i C_i \frac{\partial \Phi}{\partial Y} \quad (8.31)$$

According to the Debye approximation (for $\Phi < 27\text{mV}$) [18], there is a non-linear relation between the electric potential (Φ) and the normal direction Y to the membrane:

$$\Phi = \Phi_w e^{-k_{Db} Y} \quad (8.32)$$

where k_{Db} is the reciprocal of the Debye length. At 25°C, k_{Db} is given by:

$$k_{Db} = 3.28 \times 10^9 \times I^{0.5} \quad (8.33)$$

where I is the ionic strength in molL^{-1} .

The mass boundary conditions (Figure 8.5) are:

$$\begin{cases} C_i = C_i^0 \rightarrow Y = \delta \\ C_i = C_i^m \rightarrow Y = 0 \end{cases} \quad (8.34)$$

where C_i^0 is the concentration of component i in the feed solution, C_i^m the concentration of component i at the membrane surface and δ the thickness of the boundary layer.

Differentiating equation (8.32) in order to the vertical direction Y , an expression for $\frac{\partial \Phi}{\partial Y}$ is obtained. Then, integrating equation (8.31) with mass boundary conditions (8.34), the film equation, following a CDE model, is:

$$V_m = \frac{D_i}{\delta} \left[\ln \left(\frac{C_i^m}{C_i^0} \right) + z_i \Pi_3 [1 - \exp(-k_{Db} \delta)] \right] \quad (8.35)$$

and taking non-dimensional variables is:

$$v_m = \frac{Sh_i}{Pe_i} \left[\ln(c_i^m) + z_i \Pi_3 \left[1 - \exp \left(-\frac{k_{Db} H}{Sh_i} \right) \right] \right] \quad (8.36)$$

where Sh_i is the Sherwood number of component i , v_m the normalized velocity at the membrane surface and c_i^m the normalized concentration of component i at the membrane surface.

Sherwood number is defined as:

$$Sh_i = \frac{k_i H}{D_i} \quad (8.37)$$

where k_i is the mass transfer coefficient of component i given, according to the film equation, by:

$$k_i = \frac{D_i}{\delta} \quad (8.38)$$

Film equation (8.36) has practical utility if Sherwood number of an impermeable cell (Sh_i^I) can be used:

$$Sh_i^I = \frac{k_i^I H}{D_i} \quad (8.39)$$

k_i^I is the mass transfer coefficient of a component i in an impermeable cell.

Then:

$$v_m = \frac{Sh_i^I}{Pe_i} \left[\ln(c_i^m) + z_i \Pi_3 \left[1 - \exp\left(-\frac{k_{Db} H}{Sh_i^I}\right) \right] \right] \quad (8.40)$$

8.4.3.2. Transmission of the components and constant electric field (II)

The other film equation (**II**) based on a CDE model was established considering transmission of the components through the membrane. The constant electric field (E_f) is defined by:

$$\frac{\partial \Phi}{\partial Y} = -E_f \quad (8.41)$$

or after normalization:

$$\frac{\partial \phi}{\partial y} = -E \quad (8.42)$$

where the non-dimensional number E is given by:

$$E = \frac{E_f H}{\Phi_w} \quad (8.43)$$

Supposing constant electric field, equation (8.41), the mass balance near the membrane surface becomes:

$$V_m C_i = -D_i \frac{\partial C_i}{\partial Y} - \mu_i (-E_f) (C_i - C_i^p) + V_m C_i^p \quad (8.44)$$

The membrane is selective to the components. The concentration of component i in the permeate side, C_i^p , depends on the concentration at the membrane surface, C_i^m , and also on the rejection coefficient of component i , R_i :

$$C_i^p = C_i^m (1 - R_i) \quad (8.45)$$

Then, replacing C_i^p by $C_i^m (1 - R_i)$ and integrating equation (8.44) with mass boundary conditions (8.34), the film equation **II**, following a CDE model, is:

$$V_m - \mu_i E_f = \frac{D_i}{\delta} \left[\ln \left(\frac{R_i C_i^m}{C_i^0 - (1 - R_i) C_i^m} \right) \right] \quad (8.46)$$

After normalization the film equation becomes:

$$v_m - \frac{\mu_i E_f}{V_0} = \frac{Sh_i}{Pe_i} \left[\ln \left(\frac{R_i c_i^m}{1 - (1 - R_i) c_i^m} \right) \right] \quad (8.47)$$

Equation (8.47) also requires the use of the Sherwood number of an impermeable cell (Sh_i^I) for practical purposes:

$$v_m - \frac{\mu_i E_f}{V_0} = \frac{Sh_i^I}{Pe_i} \left[\ln \left(\frac{R_i c_i^m}{1 - (1 - R_i) c_i^m} \right) \right] \quad (8.48)$$

For a binary solution, an equation for the apparent selectivity can be derived from equation (8.48):

$$\sigma_{ap} = \frac{(1 - R_{LYS}) \exp \left[\frac{Pe_{LYS}}{Sh_{LYS}^I} \left(v_m - \frac{\mu_{LYS} E_f}{V_0} \right) \right] \left\{ R_{BSA} + (1 - R_{BSA}) \exp \left[\frac{Pe_{BSA}}{Sh_{BSA}^I} \left(v_m - \frac{\mu_{BSA} E_f}{V_0} \right) \right] \right\}}{(1 - R_{BSA}) \exp \left[\frac{Pe_{BSA}}{Sh_{BSA}^I} \left(v_m - \frac{\mu_{BSA} E_f}{V_0} \right) \right] \left\{ R_{LYS} + (1 - R_{LYS}) \exp \left[\frac{Pe_{LYS}}{Sh_{LYS}^I} \left(v_m - \frac{\mu_{LYS} E_f}{V_0} \right) \right] \right\}} \quad (8.49)$$

8.4.3.3. Evaluation of the accuracy of the film equation

The accuracy of the film equation can be evaluated by comparing the Sherwood number for an impermeable system, Sh_i^I , with the Sherwood number given by the film equation, Sh_i^{ln} . In the case of the film equation **I**, the following equation is used:

$$Sh_i^{ln} = \frac{v_m Pe_i}{\ln(c_i^m) + z_i \Pi_3 \left[1 - \exp \left(-\frac{k_{Db} H}{Sh_i^{ln}} \right) \right]} \quad (8.50)$$

If electric interactions are negligible, equation (8.50) becomes:

$$Sh_i^{ln} = \frac{v_m Pe_i}{\ln(c_i^m)} \quad (8.51)$$

In the case of film equation **II**, the Sherwood number given by the film equation is:

$$Sh_i^{ln} = \frac{\left(v_m - \frac{\mu_i E_f}{V_0} \right) Pe_i}{\ln \left(\frac{R_i c_i^m}{1 - (1 - R_i) c_i^m} \right)} \quad (8.52)$$

If electric effects are negligible:

$$Sh_i^{ln} = \frac{v_m Pe_i}{\ln \left(\frac{R_i c_i^m}{1 - (1 - R_i) c_i^m} \right)} \quad (8.53)$$

The values of c_i^m and v_m are determined by the numerical code. This code takes into account the considerations cited in the previous section: total rejection of the components (**I**) or constant electric field (**II**). Equations (8.51) and (8.53) are identical to the conventional film equation obtained from the CD model.

8.5. Results and discussion

8.5.1. Range of applicability of the film equation

The Sherwood numbers of the components along the length of the membrane x , predicted by equations (8.50) and (8.52), are going to be compared with the Sherwood numbers in an impermeable cell. This comparison is done to study the range of applicability of the film equation. The effect of the electrical interactions on the applicability of each film equation was determined by studying the effect of the non-dimensional numbers $|z_i \times \Pi_3|$ (for film equation **I**) or $|z_i \times E|$ (for film equation **II**).

8.5.1.1. Non-linear electric field (**I**)

Sherwood number profiles of BSA and LYS are represented in Figures 8.6a and 8.6b. Three Sherwood profiles are represented: the Sherwood number determined by the film equation based in a CD model - equation (8.51), the film equation based on a CDE model – equation (8.50), and the Sherwood number for an impermeable cell. While the Sherwood

number profiles based on the CDE model are coincident with the Sherwood number for an impermeable cell, the Sherwood numbers obtained by the CD model are higher (BSA) or lower (LYS). This behaviour stresses the importance of the electric effects to make predictions with the film equation.

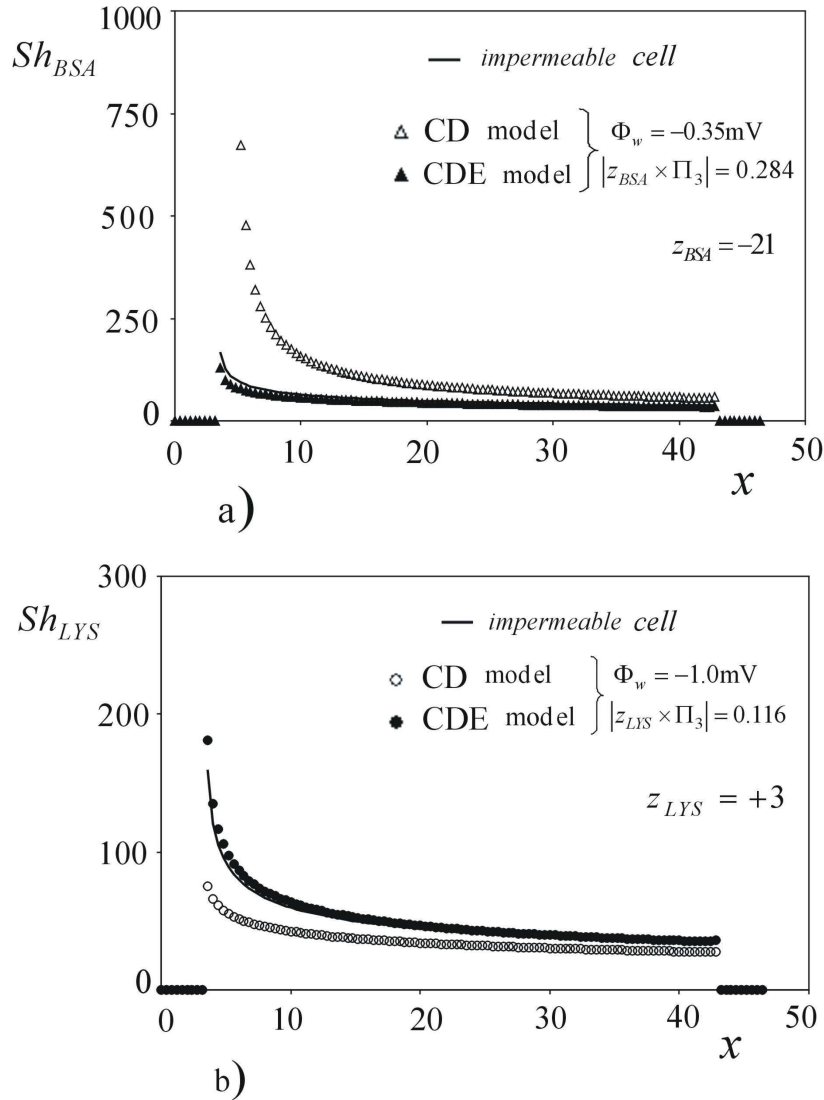


Figure 8.6 – Sherwood number along the length of the membrane, x , determined through film equations (CD and CDE model – film equation **I**): a) BSA; b) LYS and ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4$ Pa).

The accuracy of the film equation (**I**) depends on the non-dimensional number $|z_{BSA} \times \Pi_3|$. Figure 8.7 shows the Sherwood number profiles of BSA and LYS, determined by equation (8.50). Total rejection of both components was considered in the

numerical calculations. Figures 8.7a and 8.7b show Sherwood profiles for low zeta-potential values of a negatively charged membrane. Figures 8.7c and 8.7d represent the respective Sherwood profiles for high zeta-potential values of the negatively charged membrane. When the non-dimensional number $|z_{BSA} \times \Pi_3|$ is lower than 0.284 (Figure 8.7a), the Sherwood profiles of BSA are independent of the electric potential at the membrane surface and they are equal to the Sherwood number profile in an impermeable cell.

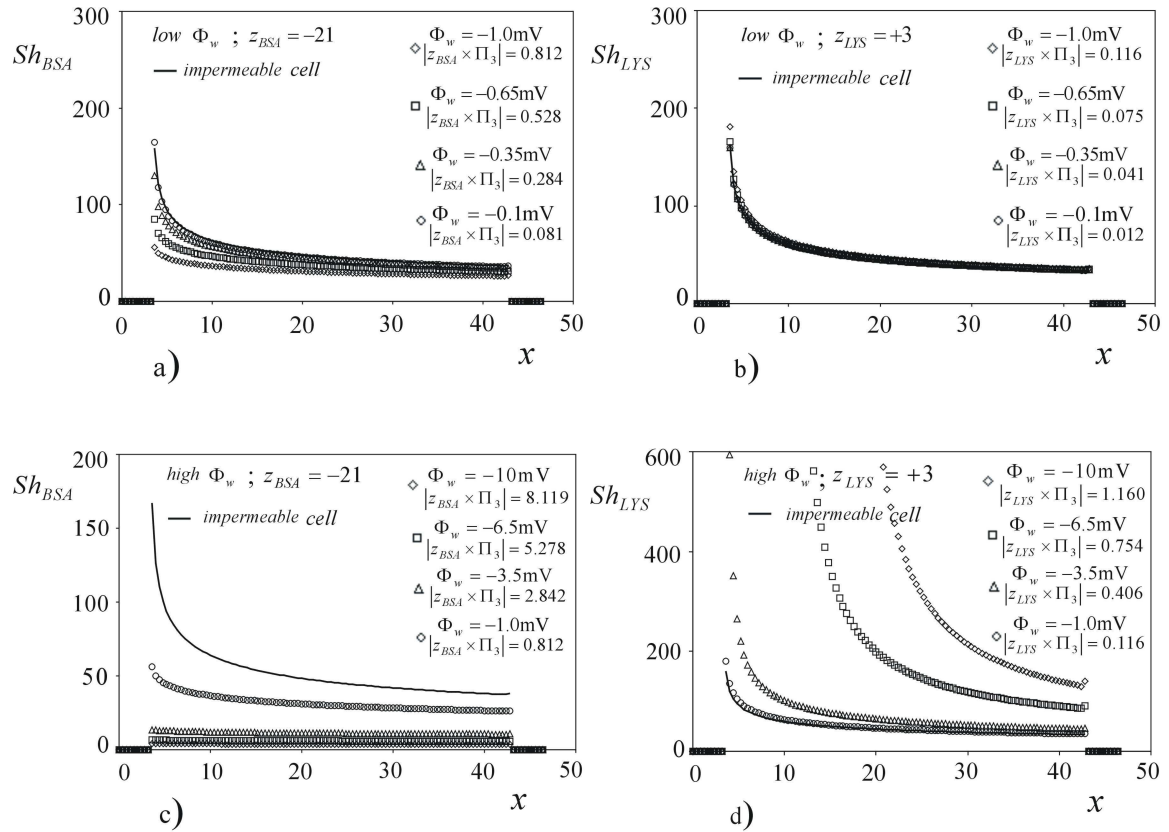


Figure 8.7 – Sherwood number along the length of the membrane, x , determined thought film equation **I**: a) for BSA and low zeta-potential values at the membrane surface; b) for LYS and low zeta-potential values at the membrane surface; c) for BSA and high zeta-potential values at the membrane surface; d) for LYS and high zeta-potential values at the membrane surface. ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4$ Pa).

When the non-dimensional number $|z_{BSA} \times \Pi_3|$ is higher, for example $|z_{BSA} \times \Pi_3| = 8.119$ (Figure 8.7c), the membrane has a strong negative zeta-potential ($\Phi_w = -10$ mV) and the BSA a strong negative electric charge ($z_{BSA} = -21$) and so the

repulsion of BSA by the membrane is high. A maximum of BSA concentration (Figure 8.8), far from the surface and at the end of the membrane, can be observed in Figure 8.8. At the membrane surface, the normalized BSA concentrations are lower than 1, i.e. concentrations at the membrane surface are lower than concentrations in the bulk (Figure 8.8).

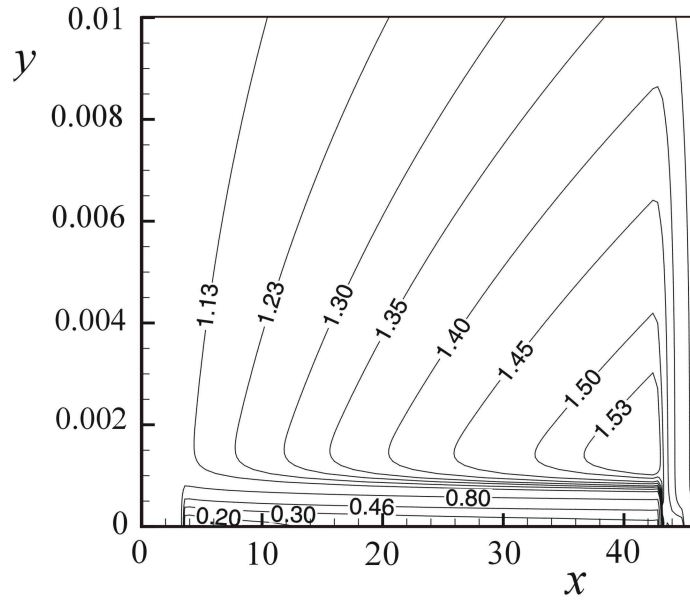


Figure 8.8 – Iso-concentration lines of BSA for $|z_{BSA} \times \Pi_3| = 8.119$ ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Phi_w = -10\text{mV}$ ($|z_{BSA} \times \Pi_3| = 8.119$ and $|z_{LYS} \times \Pi_3| = 1.160$), $\Pi_1 = 1.07 \times 10^{-4}$, $\Pi_2 = 1.36 \times 10^5$, $\Pi_3 = 0.387$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

For a non-dimensional number $|z_{LYS} \times \Pi_3|$ lower than 0.116, Figures 8.7b and 8.7d show that the Sherwood profiles of LYS overlap and are equal to the Sherwood profile in an impermeable cell. When the potential at the membrane surface is higher (for example $|z_{LYS} \times \Pi_3| = 1.160$), Sherwood number is much higher than that in an impermeable cell (Figure 8.7d). For $|z_{LYS} \times \Pi_3| = 1.160$, LYS, with electric charge equal to +3, is strongly attracted to the membrane and its concentration increases (Figure 8.9) comparatively to the concentration when $|z_{LYS} \times \Pi_3| = 0.116$.

Film equation **I** based on the CDE model is accurate, i.e. Sherwood number of an impermeable cell can be used in the film equation, for both components, when the values of the non-dimensional number $|z_i \times \Pi_3|$ are lower than 0.284.

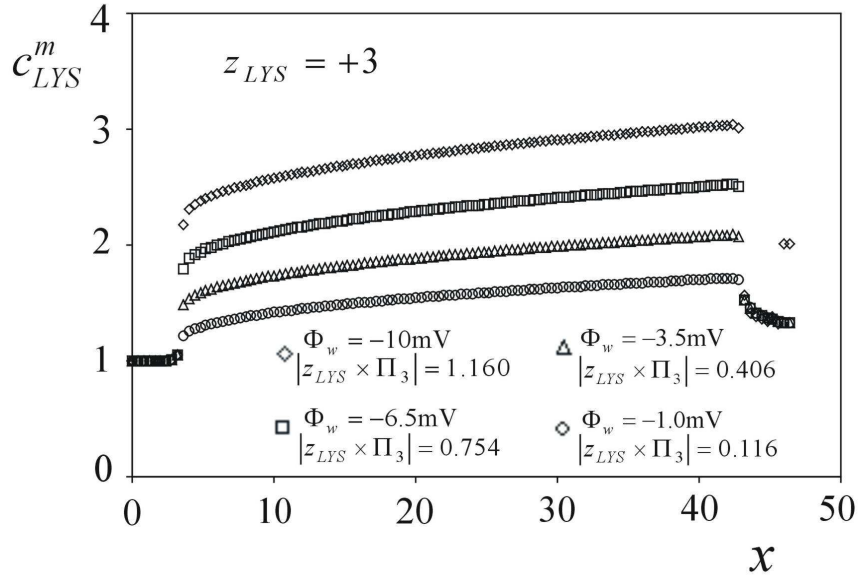


Figure 8.9 – Normalized concentration profiles of LYS along the longitudinal direction x and for different values of zeta-potential at the membrane surface: $\Phi_w = -10\text{mV}$ ($|z_{LYS} \times \Pi_3| = 1.160$), $\Phi_w = -6.5\text{mV}$ ($|z_{LYS} \times \Pi_3| = 0.754$), $\Phi_w = -3.5\text{mV}$ ($|z_{LYS} \times \Pi_3| = 0.406$), $\Phi_w = -1.0\text{mV}$ ($|z_{LYS} \times \Pi_3| = 0.116$) ($\text{Re} = 95$, $\text{Pe}_{BSA} = 1.36 \times 10^6$, $\text{Pe}_{LYS} = 8.05 \times 10^5$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4$ Pa).

8.5.1.2. Constant electric field (II)

Figure 8.10 shows Sherwood profiles of BSA and LYS along the surface of the membrane for a constant electric field. Three profiles are represented: the Sherwood number determined by the film equation based on the CD model, equation (8.53), the Sherwood number determined by the film equation based on the CDE model, equation (8.52) and the Sherwood number for an impermeable cell.

The Sherwood profiles determined by the film equation based on the CDE model are coincident with the Sherwood for an impermeable cell. The film equation, based on the CD model, overpredicts (BSA) or underpredicts (LYS) the Sherwood for an impermeable cell. This behaviour illustrates the importance of the electric term of the film equation.

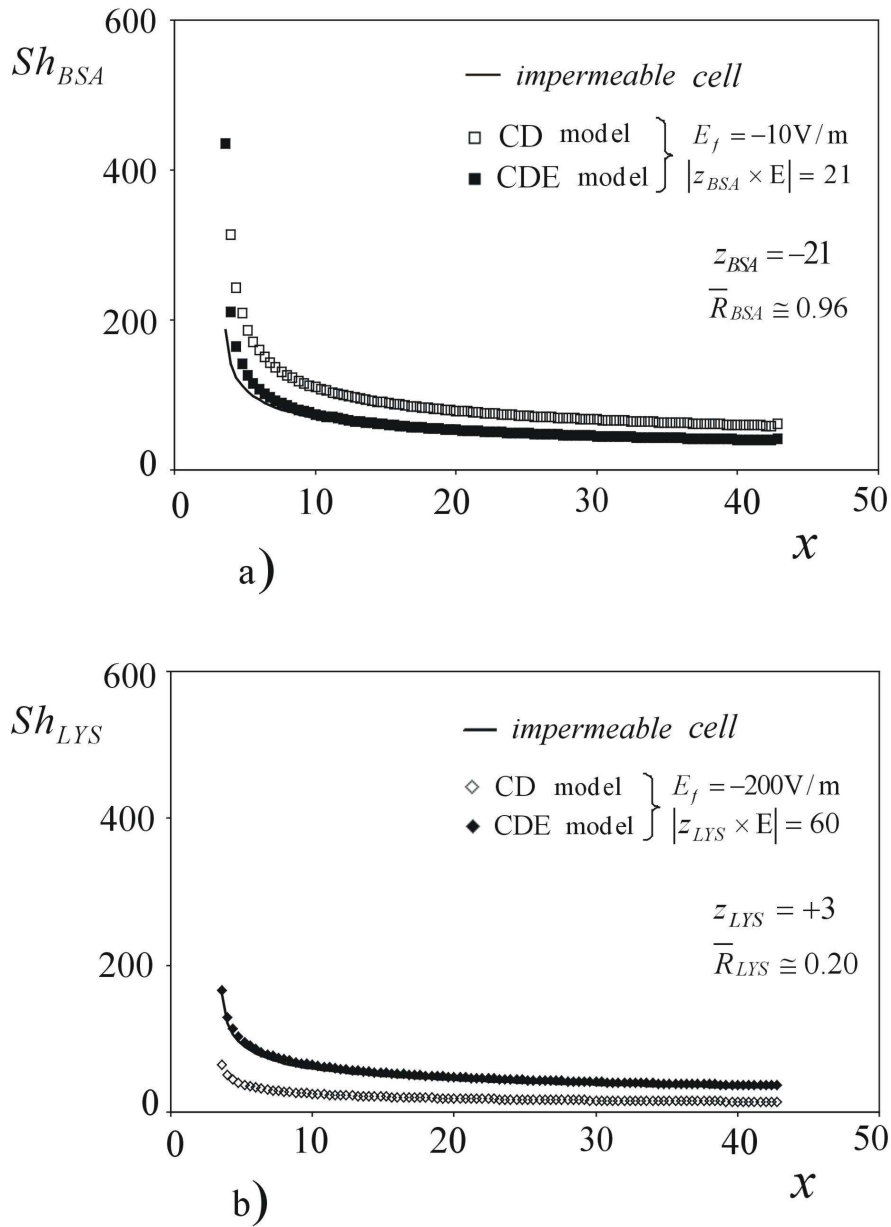


Figure 8.10 – Sherwood number along the length of the membrane, x , determined through film equations (CD and CDE model – film equation **II**) a) BSA; b) LYS ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

Film equation **II** was used to determine the Sherwood profiles along the membrane for several values of constant electric field. Sherwood number profiles for BSA (for $x > 8$ - Figure 8.11a) and LYS (Figure 8.11b) along the longitudinal direction x are coincident for E_f between -0.1 V/m and -200 V/m . The Sherwood profiles are also identical to those in an impermeable cell (Figure 8.11a and 8.11b).

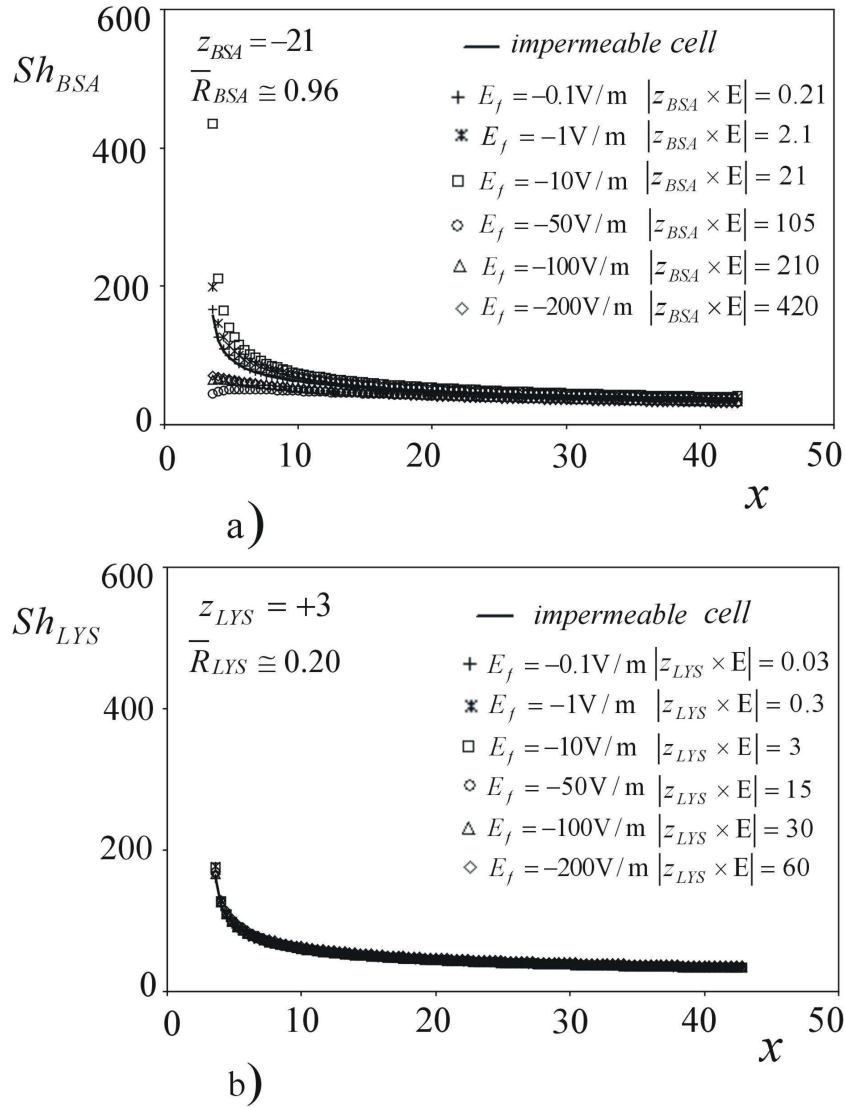


Figure 8.11 – Sherwood number profiles along the length of the membrane, x , determined through film equation **II** for: a) BSA; b) LYS; and different values of constant electric field: $E_f = -0.1V/m$, $E_f = -1V/m$, $E_f = -10V/m$, $E_f = -50V/m$, $E_f = -100V/m$, $E_f = -200V/m$ ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4$ Pa).

Nevertheless, a short non-overlapping of BSA Sherwood profiles (Figure 8.11a) at the beginning of the membrane ($x < 8$) is observed. Film equation **II** is not accurate for $x < 8$ when $|z_{BSA} \times E| \geq 105$. For $|z_{BSA} \times E| \leq 21$, the profiles are similar to those in an impermeable cell (Figure 8.11a) and the film equation is applicable along the total length of the membrane. The inaccuracy of the film equation for $|z_{BSA} \times E| \geq 105$ is associated with low BSA concentrations at the membrane surface (Figure 8.12). Since the repulsion of BSA from the membrane is high, the concentration over the membrane surface is much lower than the

concentration in the bulk (normalized concentration lower than 1 - Figure 8.12) and it decreases along the membrane surface (Figure 8.12).

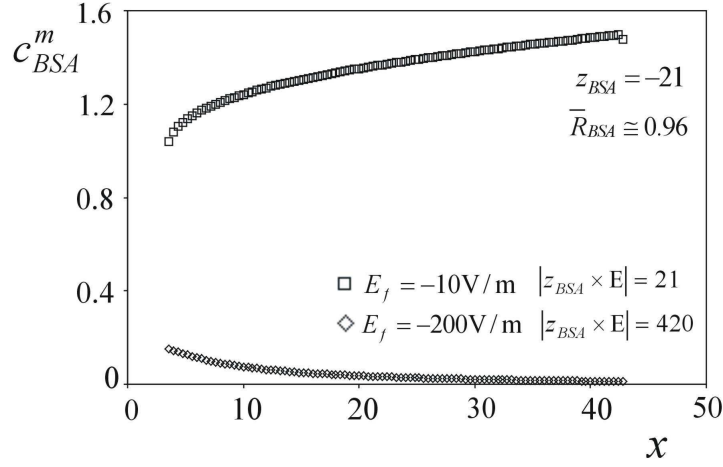


Figure 8.12 – Normalized concentration profiles of BSA along the longitudinal direction, x , of the membrane, for two values of constant electric field: $E_f = -10 \text{ V/m}$ ($|z_{BSA} \times E| = 21$);

$E_f = -200 \text{ V/m}$ ($|z_{BSA} \times E| = 420$) ($\text{Re} = 95$, $\text{Pe}_{BSA} = 1.36 \times 10^6$, $\text{Pe}_{LYS} = 8.05 \times 10^5$,

$\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

For values of $|z_{LYS} \times E| \leq 60$ (Figure 8.10b), the LYS concentration at the membrane surface increases moderately along the length of the membrane (Figure 8.13).

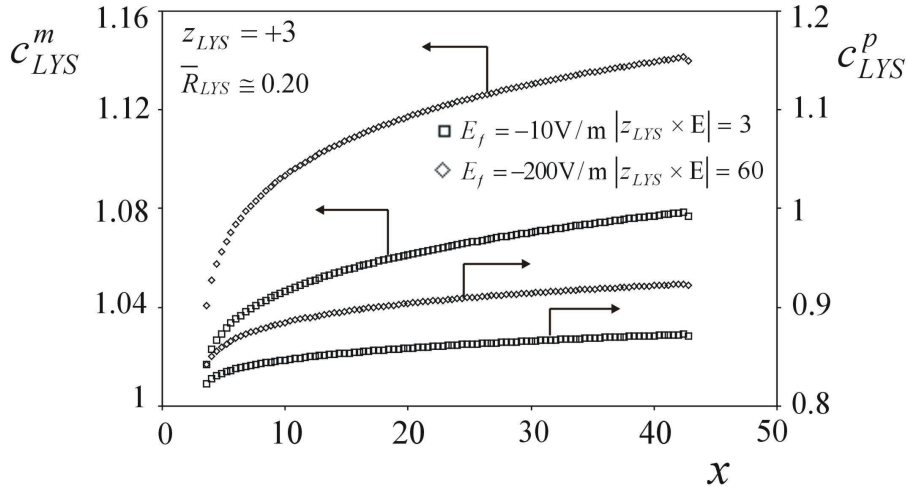


Figure 8.13 – Normalized concentration profiles of LYS at the membrane surface and in the permeate stream along the tangential direction, x , for two values of constant electric field:

$E_f = -10 \text{ V/m}$ ($|z_{LYS} \times E| = 3$) and $E_f = -200 \text{ V/m}$ ($|z_{LYS} \times E| = 60$) ($\text{Re} = 95$, $\text{Pe}_{BSA} = 1.36 \times 10^6$,

$\text{Pe}_{LYS} = 8.05 \times 10^5$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

Since LYS has an electric charge +3, its attraction to the negatively charged membrane surface is not so strong compared to the repulsion of BSA. LYS is also the component with higher transmission through the membrane.

8.5.2. Prediction of the selectivity by the film equation

Figure 8.14 shows the apparent selectivity of the separation of BSA and LYS in an ionic solution of NaCl, along the length of the membrane, for two values of the electric field. The apparent selectivity was determined by equation (8.49). This output is compared with the one obtained by the numerical code.

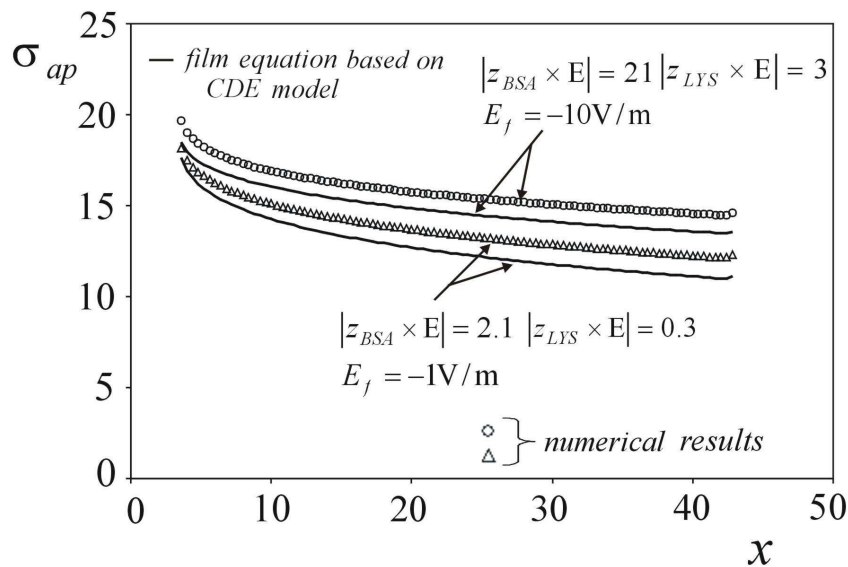


Figure 8.14 – Apparent selectivity along the length of the membrane, x , for two different values of constant electric field: $E_f = -10 \text{ V/m}$ and $E_f = -1 \text{ V/m}$ ($\text{Re} = 95$, $\text{Pe}_{\text{BSA}} = 1.36 \times 10^6$,

$$\text{Pe}_{\text{LYS}} = 8.05 \times 10^5, \text{Pe}_{\text{Na}^+} = 7.14 \times 10^4, \text{Pe}_{\text{Cl}^-} = 4.68 \times 10^4, \Delta P_0 = 1 \times 10^4 \text{ Pa}).$$

The apparent selectivity determined by equation (8.49) has a mean relative deviation around 6% relatively to the apparent selectivity determined by the numerical code. This deviation is mainly due to the differences observed in the concentration profiles of BSA at the membrane surface and in the permeate stream – mean relative deviation of 6.3% (Figure 8.15a). For LYS, the mean relative deviation in the concentration profiles is only 0.06% (Figure 8.15b). The concentration of BSA is higher when obtained from the film equation **II** (Figure 8.15a). Consequently, the apparent selectivity of the separation, equation (8.1), is

lower (Figure 8.14), since BSA is the most retained component ($\bar{R}_{BSA} \cong 0.96$). In spite of this behaviour, equation (8.49) gives good predictions of the apparent selectivity.

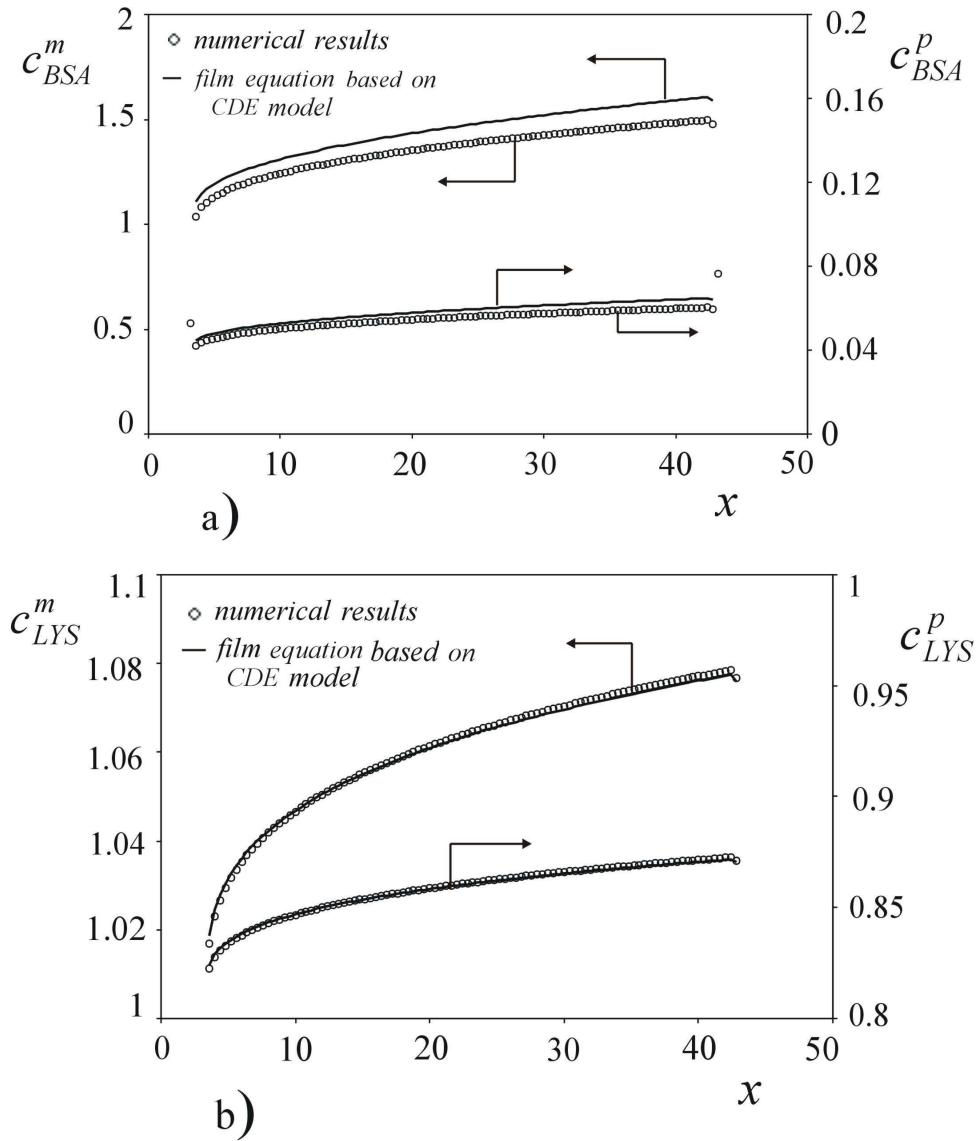


Figure 8.15 – Normalized concentration profiles at the membrane surface and in the permeate stream along the tangential direction, x , of a) BSA; b) LYS; considering a constant electric field $E_f = -10 \text{ V/m}$ ($|z_{BSA} \times E| = 21$ and $|z_{LYS} \times E| = 3$) ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

Since equation (8.49) gives a good approximation, the effect of the electric interactions between membrane and components in the apparent selectivity was also analysed. The apparent selectivity increases (Figure 8.14) for increasing values of the non-dimensional numbers $|z_{BSA} \times E|$ and $|z_{LYS} \times E|$, i.e., for stronger electric interactions (Figure 8.14). BSA has

a strong negative electric charge (-21) and LYS a moderate positive electric charge (+3). Therefore, for increasing negative zeta-potentials at the membrane surface, the repulsion between BSA and the membrane and the attraction of LYS to the membrane surface are stronger. Consequently, the transmission of LYS increases and the transmission of BSA decreases.

Moreover, the apparent selectivity using a negatively charged membrane increases 17% relatively to the apparent selectivity without any electric interactions (Figure 8.16). However, when a positively charged membrane is used, the apparent selectivity of the separation decreases 14% (Figure 8.16). In this case, BSA (with electric charge equal to -21) is attracted to the membrane and so, the transmission of BSA increases (Figure 8.17a). LYS, with positive electric charge equal to +3, is repelled from the positively charged membrane and the transmission of this component decreases (Figure 8.17b). Therefore, the apparent selectivity decreases (Figure 8.16).

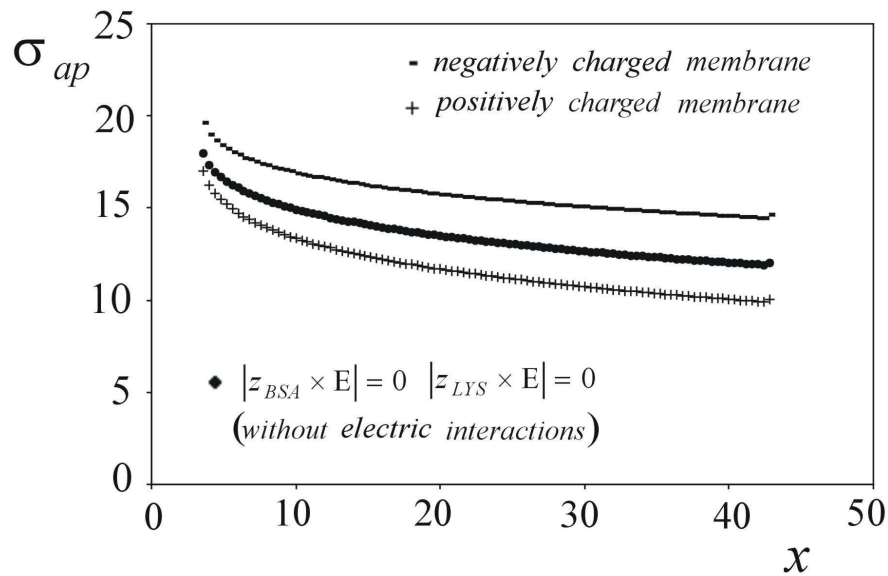


Figure 8.16 – Apparent selectivity along the length of the membrane x , considering a negatively charged membrane ($E_f = -10\text{V/m}$), a positively charged membrane ($E_f = 10\text{V/m}$) and a neutral membrane ($|z_{BSA} \times E| = 0$ and $|z_{LYS} \times E| = 0$); ($Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

In summary, the apparent selectivity of the separation of two components increases when the component with the highest transmission through the membrane is the most attracted to the membrane surface due to electric interactions. In the study developed, both mechanisms determine the apparent selectivity of the separation; the effects of transmission through the membrane and of the electric interactions are convergent when a negatively charged membrane is used.

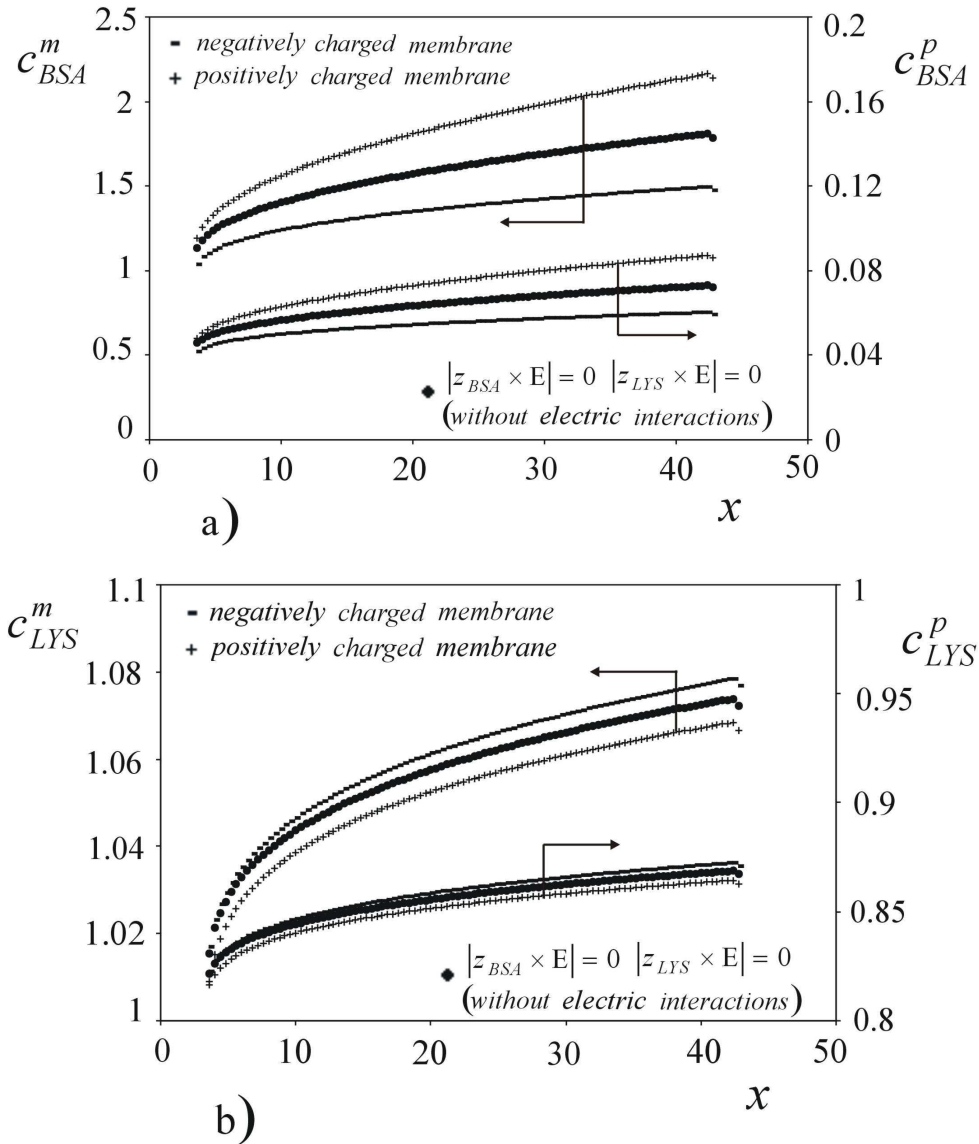


Figure 8.17 – Normalized concentration profiles at the membrane surface and in the permeate stream along the tangential direction, x , of: a) BSA; b) LYS; considering a negatively charged membrane ($E_f = -10\text{V/m}$), a positively charged membrane ($E_f = 10\text{V/m}$) and a neutral membrane ($|z_{BSA} \times E| = 0$ and $|z_{LYS} \times E| = 0$); ($\text{Re} = 95$, $\text{Pe}_{BSA} = 1.36 \times 10^6$, $\text{Pe}_{LYS} = 8.05 \times 10^5$, $\text{Pe}_{Na^+} = 7.14 \times 10^4$, $\text{Pe}_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

8.6. Conclusions

Two versions of the film equation based on a convective-diffusive-electrophoretic migration (CDE) model were developed: one supposing a non-linear relation of the electric potential along the normal direction Y – film equation **I**.; other considering a constant electric field – film equation **II**.

The applicability of the film equations was studied. Sherwood number profiles of BSA and LYS, along the length of the membrane, obtained with the film equations were compared with the Sherwood number profile of an impermeable cell. Normalized concentrations, normalized permeate velocities and rejection coefficients along the length of the membrane, obtained though the numerical code, were used as input into the film equations.

For the film equation **I**, the Sherwood number returned by the film equation is independent of the electric potential at the membrane surface (Φ_w) for values of non-dimensional number $|z_i \times \Pi_3|$ lower than 0.284. Considering constant electric field, film equation **II**, Sherwood number profile is also independent of the constant electric field (E) along the membrane, for an extended range of the non-dimensional number $|z_i \times E|$, between 0.03 and 420. For both ranges of the non-dimensional numbers, $|z_i \times \Pi_3|$ and $|z_i \times E|$, Sherwood number profiles are also equal to that in an impermeable cell. The film equations, with Sh_i^I , are then accurate for these ranges.

Film equation **II** gives good predictions of the apparent selectivity of the separation of BSA and LYS in an ionic solution of NaCl. The mean difference, along the total length of the membrane, observed between the apparent selectivity determined by the film equation **II** and the one determined by the numerical code is 6%.

Since this difference is low, the importance of membrane-components electric interactions in the apparent selectivity was also studied, taking film equation **II**. The apparent selectivity increases when the membrane has the same electric signal charge as the component with the highest rejection coefficient; in the specific case, when membrane is

negatively charged, since BSA (most retained component) has a negative electric charge. The separation promoted by the membrane pores and the separation promoted by the electric interactions have a cumulative effect and so the apparent selectivity increases. This increase becomes significant when the electric interaction between membrane and components is high, i.e., for increasing values of the non-dimensional number $|z_i \times E|$.

8.7. Nomenclature

C_i	Concentration of component i
c_i	Normalized concentration of component i
$c_{g,h}^k$	Normalized concentration of a component in a node (g,h) at a current iteration k
C_i^0	Concentration of component i at the feed/bulk
c_i^0	Normalized concentration of component i at the feed/bulk
C_{ref}^0	Concentration of the reference component at the feed/bulk
c_{ref}^0	Normalized concentration of the reference component at the feed/bulk
$C_{M,i}^0$	Molar concentration of component i at the feed/bulk
$c_{M,i}^0$	Normalized molar concentration of component i at the feed/bulk
C_i^m	Concentration of component i at membrane surface
c_i^m	Normalized concentration of component i at membrane surface
C_i^p	Concentration of component i in the permeate flux
c_i^p	Normalized concentration of component i in the permeate flux
$c_{i,crit}^k$	Normalized concentration of component i on a critical location
D_i	Molecular diffusivity of component i
$D_{i,eff}$	Effective diffusivity of component i along the membrane pores
E_f	Constant electric field
F	Faraday constant
H	Distance between parallel plates
I	Ionic strength

k	Current time step
k_i	Mass transfer coefficient of component i
k_i^I	Mass transfer coefficient of component i in an impermeable cell
k_{Db}	Reciprocal of the Debye length
L_{out}	Length of the outlet section
L_{in}	Length of the inlet section
L_m	Total length of the membrane
L	Total length of the cell
M_i	Molar mass of component i
M_{ref}	Molar mass of the reference component
R	Gas constant
R_i	Local rejection coefficient of component i
$\overline{R}_i$	Mean rejection coefficient of component i along the total length of the cell
$R_{g,1}$	Rejection coefficient of a component in a node $(g,1)$ at membrane surface
R_m	Membrane resistance of the semi-permeable membrane
R_ϕ	Sum of the residues of the electric potential equation
r_e	Sum of the normalized ionic concentrations
r_i^*	Equivalent molecular radius of component i
S_{ap_i}	Apparent sieving coefficient of component i
S_i	Real transmission of component i
$S_{i,\infty}$	Asymptotic intrinsic sieving coefficient of component i
s	Specific area of the pores of the membrane
T	Temperature
t	Non-dimensional time
V_0	Mean feed velocity
V_x	Longitudinal component of the velocity
v_x	Normalized longitudinal component of the velocity
$\hat{v}_{xi}$	Normalized pseudo-velocity in longitudinal direction, x , of component i
V_y	Vertical component of the velocity
v_y	Normalized vertical component of the velocity

V_m	Velocity at membrane surface (vertical component)
v_m	Normalized velocity at membrane surface (vertical component)
$\hat{v}_{y_i}$	Normalized pseudo-velocity in vertical direction, y , of component i
$\hat{v}_{y_{g,h}}$	Normalized pseudo-velocity (component y) in a node (g,h)
$\hat{v}_{y_{g,1}}$	Normalized pseudo-velocity (component y) in a node $(g,1)$
$\hat{v}_{yu}^m$	Incoming pseudo-velocity (normal direction) to the discretized node $(g,1)$ at membrane surface
$\hat{v}_{yd}^m$	Outgoing pseudo-velocity (normal direction) from the discretized node $(g,1)$ at membrane surface
W	Width of the cell
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Y	Vertical coordinate
y	Normalized vertical coordinate
z_i	Electric charge of component i

Non-dimensional numbers

Pe_i	Peclet number of component i
Re	Reynolds number of the solution
Sh_i	Sherwood number of component i
Sh_i^I	Sherwood number of component i in an impermeable cell
Sh_i^{ln}	Sherwood number of component i given by film equation
E	Non-dimensional number defined by equation 43
Π_1	Non-dimensional number defined by equation 8
Π_2	Non-dimensional number defined by equation 5
Π_3	Non-dimensional number defined by equation 18

Greek Symbols

ΔP_0	Static pressure difference across the semi-permeable membrane
Δt	Time step range
Δy	Step range at normal direction
ε	Permittivity
$\varepsilon_{ci_{crit}}$	Numerical error of the concentration of component i on a critical location
$\varepsilon_{\phi_{crit}}$	Numerical error of the electric potential on a critical location
$\varepsilon_{\omega_{crit}}$	Numerical error of the vorticity on a critical location
ψ	Stream function
ω	Vorticity
ω_{crit}^k	Vorticity on a critical location
ρ	Density
μ_i	Electrophoretic mobility of component i
$\bar{\mu}$	Mean viscosity of the solution
$\bar{\mu}_p$	Mean viscosity at the permeate flux
δ_m	Membrane thickness
δ	Thickness of the boundary layer
σ_{ap}	Apparent selectivity
Φ	Electric potential
ϕ	Normalized electric potential
Φ_w	Membrane electric potential
ϕ_{crit}^k	Normalized electric potential on a critical location
ζ_i	Zeta-potential of component i

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Chapter 9

Conclusions and Future Work

This chapter describes the main conclusions of the thesis and the suggestions for future work.

9.1. Conclusions of the thesis

➤ Hybrid Membrane Cells combined with differential diffusion of the solutes

One of the main objectives of this thesis was to study, by numerical methods, the potential of a new membrane fractionation process based on the combination of hybrid membrane cells (HMC) and differential diffusion of two solutes. The potential of this new fractionation process was shown through the purity and recovery of the solute with lower diffusivity. The purity and recovery depends on several operational parameters such as: solvent stream velocity, concentrate stream velocity and number of sections. The purity increases with the solvent stream velocity, decreases with the concentrate velocity and increases with the number of sections. The recovery increases with the solvent stream velocity and also with the concentrate stream velocity.

Moreover, the effect of the concentration on the physical properties (viscosity of the solution and molecular diffusivity of each component) and the effect of the osmotic pressure of the solutes were studied for this new fractionation. Separation pairs of Bovine Serum Albumin (BSA) / Dextran-T10 (DT10) and BSA / Lysosyme (LYS) were considered. Purity of BSA (less diffusive component) was determined for variable physical properties (viscosity and diffusivity as a function of the concentration of the solutes) and also supposing constant properties. The purity of the separation was analyzed for low and high concentration polarization of the semi-permeable membrane surface and for different values of the permeate velocity of the concentrate stream. For low levels of concentration polarization (low applied pressure difference), the effect of variable transport properties are not important, since the separation is practically inexistent. For high levels of concentration polarization, the variation of the transport properties (viscosity increases and diffusivity decreases) influences the separation. For BSA/DT10 system, the purity of the less diffusive component (BSA) increases in the outgoing stream current i.e., in the concentrate stream. This increase can reach 20% and is even higher as lower is the concentrate velocity. For BSA/LYS system, the purity of BSA decreases when variable transport properties are taken on account. The BSA purity decrease can reach 6% of the separation.

➤ Selective Hybrid Membrane Cells

The potential of a new fractionation process combining hybrid membrane cells and selective semi-permeable membranes was explored. However, before achieving this main

objective, the effect of several operational parameters in the apparent selectivity of a conventional cell was studied in detail.

The fractionation of two components (BSA and DT10) by ultrafiltration in a conventional cell was studied considering a convective-diffusive model to simulate the transmission of the components through the membrane pores. The study took on account the pressure drop in the cell, the variation of the permeate velocity along the cell, the concentration polarization over the membrane, the variation of the transport properties and the variation of the osmotic pressure with the concentration of the solutes. The apparent selectivity was determined in order to study the effect of the transmembrane pressure, Reynolds number, inlet solutes concentration, specific area of the membrane pores and resistance of the membrane. When the pressure drop is negligible, the apparent selectivity increases with the increasing of the transmembrane pressure until it reaches a maximum after which decreases. When the pressure drop along the cell is significant, the first half of the curve is not observed. The mean apparent selectivity increases with increasing Reynolds number due to the concentration polarization phenomena. For a given transmembrane pressure, the apparent selectivity increases with the decrease of the area of the pores and with the increase of the resistance of the membrane. For low inlet concentration of the components, the variation of the physical properties does not have any effect in the apparent selectivity. For high inlet concentrations and high values of the transmembrane pressure, the effect of the variable physical properties is appreciable and the apparent selectivity decreases.

The apparent selectivity of the fractionation process of two macromolecules (BSA and DT10) was also obtained, by numerical methods, using a selective HMC (one of the main objectives of the thesis). The results show that fully permeable membranes clean mass boundary layer over the semi-permeable membranes, reducing concentration polarization and the transmission of the components. Consequently, when HMC are used, the apparent selectivity through the semi-permeable membranes increases. For a range of high transmembrane pressure (where a conventional membrane polarizes) the apparent selectivity in a hybrid membrane cell is high. This selectivity in a HMC increases, increasing the velocity of the concentrate stream and the number of sections. At high concentration polarization levels, hybrid membrane cells do not only have a high apparent selectivity in the semi-permeable membranes but also they have a good selectivity in the fully-permeable membranes and a high permeate velocity across the semi-permeable membranes.

➤ **Hybrid Membrane Cells with electric interactions between membrane and components**

Other main objective of this thesis was the study, by numerical methods, of a new fractionation process combining hybrid membrane cells and electric interactions between membrane and components. However, the implementation of electric interactions membrane – components required a complex numerical resolution. To achieve this objective, simplest situations were initially studied.

In a first step Poisson-Boltzmann, Nernst-Planck and Navier Stokes equations were solved. A simplified approach of Poisson-Boltzmann equation (negligible convection and binary ionic solution) was taken and the equation was solved independently. The resultant electric field was used to solve the electric terms of Nernst-Planck equations. A numerical code based on a finite volume method combining a fractional-step method and a doner-cell upwind method was developed to solve the Nernst-Planck equations. The Doner-cell upwind method, used to discretize the convective terms of Nernst-Planck equation, assures mass conservation. Fractional-step method used is sufficiently adequate and easy to implement. This method developed to solve Nernst-Planck equations was validated by comparing the numerical solution for a membrane cell containing stagnant fluid with Boltzmann equation solution (theoretical equation). The numerical code developed was used to study the mass transfer of two charged species in the vicinity of a semi-permeable negatively charged membrane. As expected, the ion with positive charge has a strong accumulation near the membrane.

Following, it was studied how to extend the new numerical code to the fractionation of two charged macromolecules in an ionic solution through a charged HMC. The Poisson-Boltzmann, Nernst-Planck and Navier-Stokes equations were solved without any simplification. The results obtained were compared with the data got with the simplified method and, for a binary ionic solution, they are very similar. When Peclet number of a component is low (high diffusivity), the convective transport is negligible relatively to the diffusive. For this condition, the results approach those for stagnant fluid. The importance of the electric terms of the vorticity equation was also studied and they do not have a significant influence in the numerical results. The new numerical code was applied to a new hybrid membrane cell which comprises negatively charged semi-permeable membranes (with total rejection of the components) and neutral fully permeable membranes. The numerical results were compared to those obtained in a hybrid membrane cell with neutral semi-permeable

membrane. If the semi-permeable membrane has the same electric signal charge than the macromolecules with higher diffusivity, these macromolecules move away further from the membrane, while those with lower diffusivity approach, further, the membrane. However, due to interactions between the electric and concentration fields in the region crossed by the streamlines of the concentrate stream, the separation in the fully-permeable membrane is lower.

The last study of this thesis, reports the application of the stagnant fluid equation to study the electrophoretic migration of proteins near ultrafiltration membranes. Two model film equations were deduced: one supposing a non-linear electric potential along the normal direction to the membrane – film equation **I**; other considering a constant electric field – film equation **II**. Sherwood number profiles of two components (BSA and LYS) along the length of the membrane were obtained, with the film equations, and compared with the Sherwood number profiles of an impermeable cell. Normalized concentrations, normalized permeate velocities and rejection coefficients obtained through the numerical code were used as input into the film equations. Film equation **I** is applicable for values of non-dimensional number $|z_i \times \Pi_3|$ lower than 0.284 and film equation **II** for values of non-dimensional number $|z_i \times E|$ between 0.03 and 420. Film equation **II** gives good predictions of the apparent selectivity of the separation of BSA and LYS both diluted in an ionic solution of NaCl. The apparent selectivity increases when the membrane has the same electric signal charge as the component with the highest rejection coefficient; in this case when membrane is negatively charged, since BSA (most retained component) has a negative electric charge. This increase is higher when electric interactions between membrane and components is also high, i.e., for increasing values of non-dimensional number $|z_i \times E|$.

9.2. Future work

➤ Selective Hybrid Membrane Cells with electric interactions between membrane and components - type D

The next step in a future work is to study the apparent selectivity of a new fractionation process combining selective hybrid membrane cells with electric interactions between membrane and components. This new type of hybrid membrane cell is composed by charged semi-permeable membranes (permeable to the solvent and partially permeable to the solutes) and neutral fully permeable membranes, as represented in Figure 9.1. Hybrid membrane cell

of Figure 9.1 is composed by two membrane sections (n). However, it can be composed by more than two.

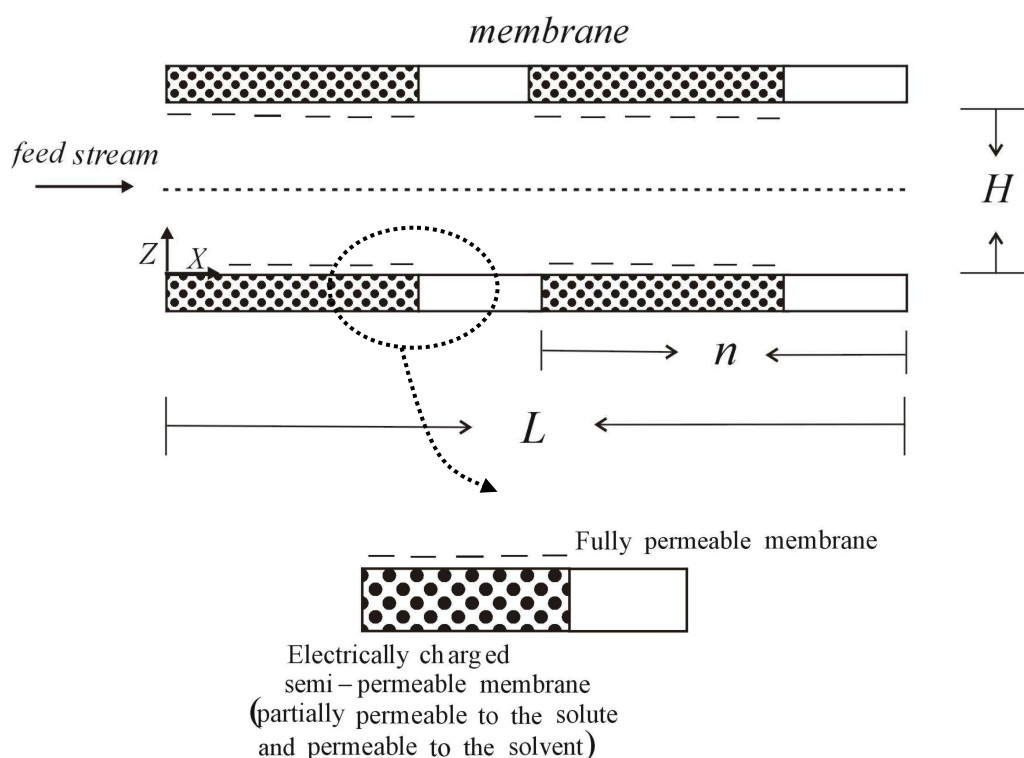


Figure 9.1 - HMC type D (with electric interactions and selective semi-permeable membranes).

Some preliminary numerical results of the apparent selectivity (considering constant electric field) along the length of this hybrid membrane cell (Figure 9.1), with four sections, are represented in Figure 9.2. The apparent selectivity of this new hybrid membrane cell is compared with the apparent selectivity of a charged conventional cell. The apparent selectivity of the charged HMC is even higher than that of a charged conventional cell. If electric interactions between membrane and components increase, the apparent selectivity using an electrically charged hybrid membrane cell can be further increased. This new type of hybrid membrane merits to be explored.

Preliminary results of apparent selectivity of Figure 9.2 were obtained for constant electric field, i.e. linear relation of the electric potential along the normal direction Y to the membrane. The apparent selectivity along the length of the charged hybrid membrane cell (Figure 9.1) should be also determined, considering a non-linear electric potential along the normal direction Y to the membrane.

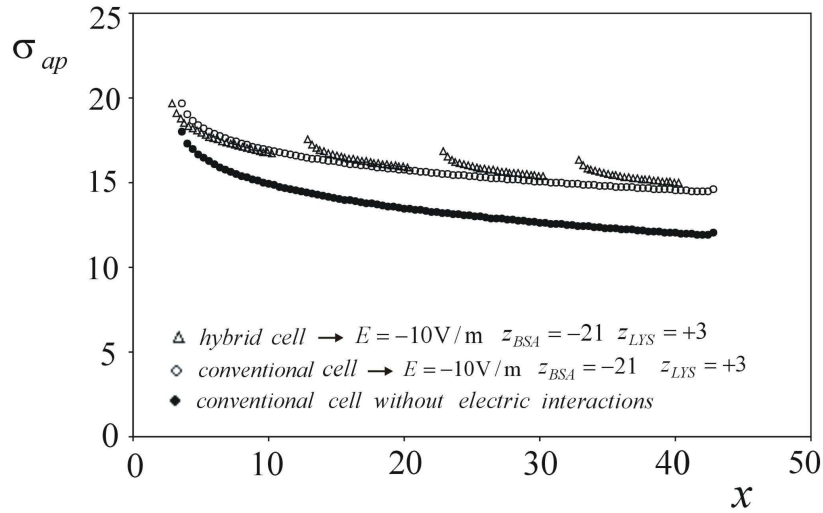


Figure 9.2 – Apparent selectivity along the membrane, x , considering a negatively charged hybrid membrane cell ($E = -10\text{V/m}$), a negatively charged conventional cell ($E = -10\text{V/m}$) and a neutral conventional cell; ($C_{BSA}^0 = 6.90 \times 10^{-5} \text{ kg/m}^3$, $C_{LYS}^0 = 1.02 \times 10^{-4} \text{ kg/m}^3$, $C_{Na^+}^0 = 2.30 \times 10^{-8} \text{ kg/m}^3$, $C_{Cl^-}^0 = 3.545 \times 10^{-8} \text{ kg/m}^3$, $z_{BSA} = -21$, $z_{LYS} = +3$, $Re = 95$, $Pe_{BSA} = 1.36 \times 10^6$, $Pe_{LYS} = 8.05 \times 10^5$, $Pe_{Na^+} = 7.14 \times 10^4$, $Pe_{Cl^-} = 4.68 \times 10^4$, $\Delta P_0 = 1 \times 10^4 \text{ Pa}$).

In this thesis, a convective-diffusive model was used (Figure 9.3a) to obtain the transmission of the components through the membrane pores. A convective-diffusive-electrophoretic migration model through the membrane pores (Figure 9.3b) should be used.

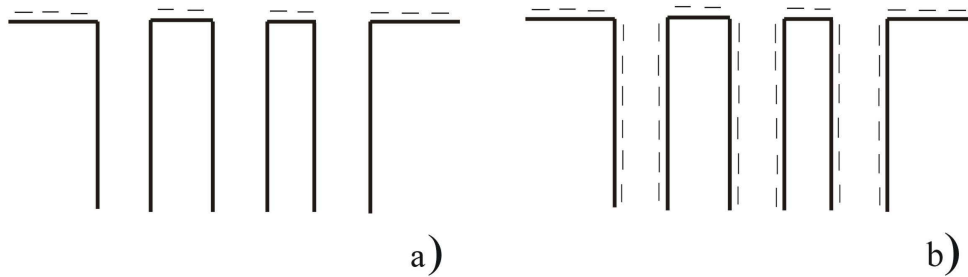


Figure 9.3 – a) Membrane with zeta-potential only at the membrane surface; b) Membrane with zeta-potential at the membrane surface and inside the membrane pores.

➤ Hybrid Membrane Cells combining reverse osmosis and pervaporation processes to separate volatile organic compounds from wastewater - type E

Another type of hybrid membrane cell that has interest to explore is the combination of pervaporation and reverse osmosis membranes, alternating in series, to separate volatile

organic components (VOC's) from wastewater. In this new fractionation process, the organic compounds are rejected and accumulated along the reverse osmosis membrane, since this membrane is only permeable to the solvent (water). Along pervaporation sections, water accumulates at the surface due to the hydrophobic characteristics of the membrane, and VOC's cross the membrane. The separation process is done by the size of macromolecules (reverse osmosis) and by the affinity of the other type of membrane relatively to VOC's (pervaporation) – Figure 9.4.

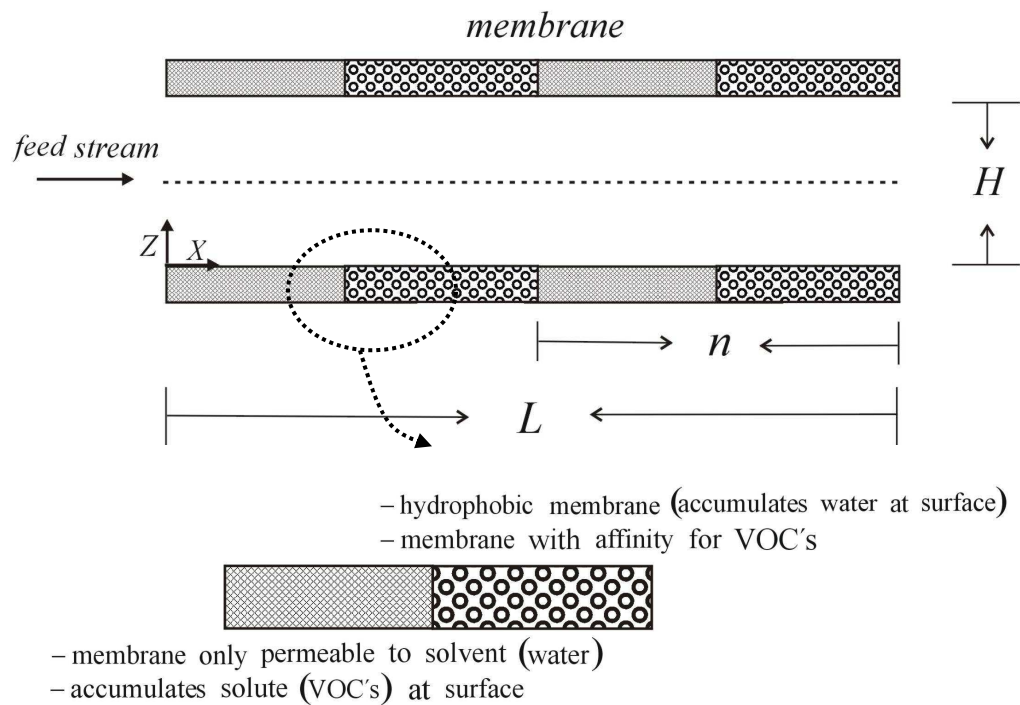


Figure 9.4 – HMC type E (combining reverse osmosis and pervaporation processes).

Appendix A

Domain and Boundary Conditions

This Appendix reports the domain of the Hybrid Membrane Cell; cell with less than four sections and also with more than four sections.

Moreover, boundary conditions of Mass Transport and Navier-Stokes equations (discretized through the finite differences method) are presented in this Appendix.

A.1. Domain

The number of grid nodes needed to accurately solve the flow and mass transport equations, increases with the number of membrane sections. As the number of nodes of the grid increases, the computational resources required become too high. This is why equations for hybrid membrane cells with four or fewer membrane sections were solved simultaneously, while hybrid membrane cells with more than four membrane sections were solved in a sequential section-by-section procedure.

For hybrid membrane cells with four or fewer membrane sections, domain A was used (Figure A.1). Domain A corresponds to half of the physical cell (the cell is symmetric) and has an inlet section, an outlet section and n membrane sections, each one with two sub-sections. The fully permeable sub-sections are usually shorter than the permeable ones. The domain was discretized and converted into a grid of discrete nodes.

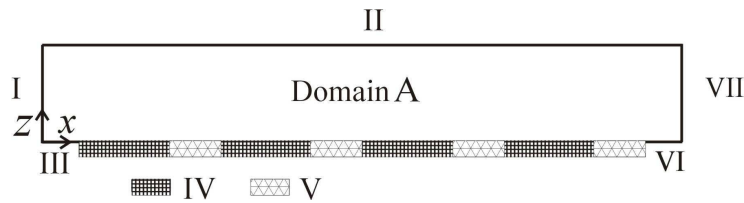


Figure A.1 – Schematic representation of domain A (cell with four or less membrane sections) and respective boundaries (I – cell inlet; II – symmetric axis; III – wall; IV – semi-permeable membrane; V – fully-permeable membrane; VI – wall; VII – cell outlet).

For hybrid membrane cells with more than four membrane sections, the flow and mass transport equations were solved sequentially, one membrane section each time. Three different domains (B, C and D), sketched in Figure A.2, were used. Domain B was used to solve the flow and mass transport equations for the first membrane section, domain C for intermediate membrane sections and domain D for the last membrane section. Consecutive domains have common regions so that mass transport across boundary sections is taken into account. The first domain solved is a B domain (module for the first section of the membrane), which corresponds to the inlet section, to the first membrane section, and to the beginning of the second membrane section. Subsequent domains are C domains (modules for the intermediate sections of the membrane) and correspond to the fully permeable sub-section of membrane section $k-1$, to membrane section k and to beginning of membrane section $k+1$. The last domain solved is a D domain (module for the last section of the

membrane) and corresponds to the fully permeable subsection of membrane section $n-1$, to last membrane section and to outlet section.

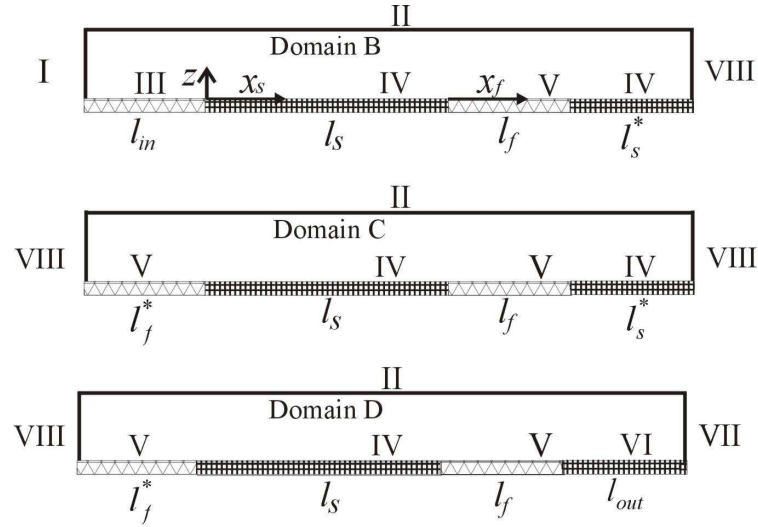


Figure A.2 – Schematic representation of domains B, C and D (for cells with more than four membrane sections) and respective boundaries (I – cell inlet; II – symmetric axis; III – wall; IV – semi-permeable membrane; V – fully-permeable membrane; VI – wall; VII – cell outlet; VIII – intermediate boundaries).

A.2. Boundary conditions

Conditions for boundaries I, II, III, VI and VII (Figures A.1 and A.2) have been presented by Miranda and Campos [1-4] and are listed in Table A.1.

The inflow values at boundary VIII of domains C and D are the outflow values of the previous sections (Table A.2).

Boundary conditions for semi-permeable membranes (boundaries IV) were analyzed by Miranda and Campos [1-4]. However, they were modified to take on account:

- a solution of two components to be separated;
- the transmission through the membrane;
- the non-linear concentration dependence of the osmotic pressure of the components;
- the concentration dependence of diffusivity and viscosity of the components.

The boundaries conditions for semi-permeable and fully permeable membranes are now presented in Table A.2.

Table A.1 - Conditions for boundaries I, II, III, VI and VII.

I	II	III	VI	VII
$v_x = \frac{3}{2} [1 - 4(0.5 - z)^2]$	$\frac{\partial v_x}{\partial z} = 0$	$v_x = 0$	$v_x = 0$	$\frac{\partial v_x}{\partial x} = 0$
$v_z = 0$	$v_z = 0$	$v_z = 0$	$v_z = 0$	$\frac{\partial v_z}{\partial x} = 0$
$\psi = \frac{3(0.5 - z)}{2} - \frac{(0.5 - z)^3}{2}$	$\psi = 0$	$\psi = \frac{11}{16}$	$\psi = \frac{11}{16} + \int -v_z dx$	$\frac{\partial \psi}{\partial x} = 0$
$\omega = 12(0.5 - z)$	$\omega = 0$	$\omega = \frac{\partial v_x}{\partial z}$	$\omega = \frac{\partial v_x}{\partial z}$	$\frac{\partial \omega}{\partial x} = 0$
$c_i = 1$	$\frac{\partial c_i}{\partial z} = 0$	$\frac{\partial c_i}{\partial z} = 0$	$\frac{\partial c_i}{\partial z} = 0$	$\frac{\partial c_i}{\partial x} = 0$
$\phi_i = 0$	$\frac{\partial \phi_i}{\partial z} = 0$	$\frac{\partial \phi_i}{\partial z} = 0$	$\frac{\partial \phi_i}{\partial z} = 0$	$\frac{\partial \phi_i}{\partial x} = 0$

Table A.2 - Semi-permeable (boundary IV) and fully permeable (boundary V) membrane boundary conditions.

IV	V	VIII
$v_x = 0$	$v_x = 0$	$v_x^k(0, z) = v_x^{k-1}(l_s + l_f, z)$
$-v_z = \frac{\Delta P - \sum_{i=1}^n \Delta \pi_i}{\bar{\mu}_p^s R_m^s V_0} = \frac{\Delta P - \sum_{i=1}^n (\pi_i^m - \pi_i^p)}{\bar{\mu}_p^s R_m^s V_0}$	$v_m^f = \frac{\Delta P^f}{\bar{\mu}_p^f R_m^f V_0}$	$v_z^k(0, z) = v_z^{k-1}(l_s + l_f, z)$
$\psi = \frac{11}{16} + \int -v_z dx$	$\psi = \frac{11}{16} + \int -v_z dx$	$\psi^k(0, z) = \psi^{k-1}(l_s + l_f, z)$
$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$	$\omega = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x}$	$\omega^k(0, z) = \omega^{k-1}(l_s + l_f, z)$
$-\frac{1}{\text{Pe}_i} \frac{\partial c_i}{\partial z} = v_m^s (c_i^m - c_i^p)$	$\frac{1}{\text{Pe}_i} \frac{\partial c_i}{\partial z} = 0$	$c_i^k(0, z) = c_i^{k-1}(l_s + l_f, z)$
$-\frac{\partial \phi_i}{\partial z} = 1$	$\frac{\partial \phi_i}{\partial z} = 0$	$\phi_i^k(0, z) = \phi_i^{k-1}(l_s + l_f, z)$

A.3. Nomenclature

C_i	Concentration of component i
c_i	Normalized concentration of component i

C_i^m	Concentration of component i at membrane surface
c_i^m	Normalized concentration of component i at membrane surface
C_i^p	Permeate concentration of component i
c_i^p	Normalized permeate concentration of component i
i	Component i
k	Section of the membrane k
L_{out}	Length of the outlet section
l_{out}	Normalized length of the outlet section
L_{in}	Length of the inlet section
l_{in}	Normalized length of the inlet section
L_s	Length of a semi-permeable membrane sub-section
l_s	Normalized length of a semi-permeable membrane sub-section
l_s^*	Part of the normalized length of the following semi-permeable membrane sub-section
L_f	Length of a fully permeable membrane sub-section
l_f	Normalized length of a fully permeable membrane sub-section
l_f^*	Part of the normalized length of the previous fully permeable membrane sub-section
n	Number of sections
R_m^s	Membrane resistance of the semi-permeable membrane
R_m^f	Membrane resistance of the fully permeable membrane
V_0	Mean feed velocity
v_m^s	Normalized permeate velocity of the semi-permeable membrane
v_m^f	Normalized permeate velocity of the fully permeable membrane
v_x	Normalized longitudinal component of the velocity
v_z	Normalized vertical component of the velocity
X	Longitudinal coordinate
x	Normalized longitudinal coordinate
Z	Vertical coordinate
z	Normalized vertical coordinate

Non-dimensional numbers

Pe_i Peclet number of component i

Greek Symbols

ΔP	Static pressure difference across a semi-permeable membrane
ΔP^f	Static pressure difference across a fully permeable membrane
π_i^m	Osmotic pressure of component i at the membrane surface
π_i^p	Osmotic pressure of component i in the permeate stream
$\Delta \pi_i$	Osmotic pressure difference of component i across the semi-permeable membrane
ψ	Stream function
ω	Vorticity
$\bar{\mu}_p^s$	Viscosity of the mixture in the stream that crosses the semi-permeable membrane
$\bar{\mu}_p^f$	Viscosity of the mixture in the stream that crosses the fully-permeable membrane
ϕ_i	$\ln(c_i)$

A.4. References

- [1] J.M. Miranda, J.B.L.M. Campos, Mass transfer in the vicinity of a separation membrane – the applicability of the stagnant film theory, *Journal of Membrane Science* 202 (2002) 137 – 150.
- [2] J.M. Miranda, J. B. L. M. Campos, An improved scheme to study mass transfer over a separation membrane, *J. Membrane Sci.* 188 (2001), 49–59.
- [3] J.M. Miranda, J.B.L.M. Campos, Numerical study of a hybrid membrane cell with semi and fully permeable membrane sub-sections, *Chemical Engineering Science*, 62 (2007) 1215-1229.

- [4] J. M. Miranda, J. B .L. M. Campos, Concentration polarisation in a membrane placed under an impinging jet confined by a conical wall—a numerical approach, *Journal of Membrane Science* 182 (2000), 257–270.

Appendix B

Discretization of mass transport equation through finite volume method

This Appendix describes the discretization method of mass transport equation (Nernst-Planck equation) with electric terms incorporated. This mass transport equation is of complex resolution. To simplify the resolution method, the equation was divided into two simpler equations with the pseudo-convective terms separated from the diffusive terms. These two shorter mass transport equations were solved sequentially through a fractional-step method. The mass transport equation with pseudo-convective terms was solved through a finite volume method combining with the donor-cell upwind method, and the mass transport equation with diffusive terms was solved through a finite volume method. Coefficients of discretized equations and boundary conditions are also presented in this Appendix.

B.1. Discretization method of mass transport equation with pseudo-convective terms

✓ Mass transport equation with pseudo-convective terms:

$$\frac{\partial c}{\partial t} + \hat{v}_x \frac{\partial c}{\partial x} + \hat{v}_y \frac{\partial c}{\partial y} = 0 \quad (\text{B.1})$$

✓ Mass balance (pseudo-convective flux):

Mass balance to the node of Figure B.1:

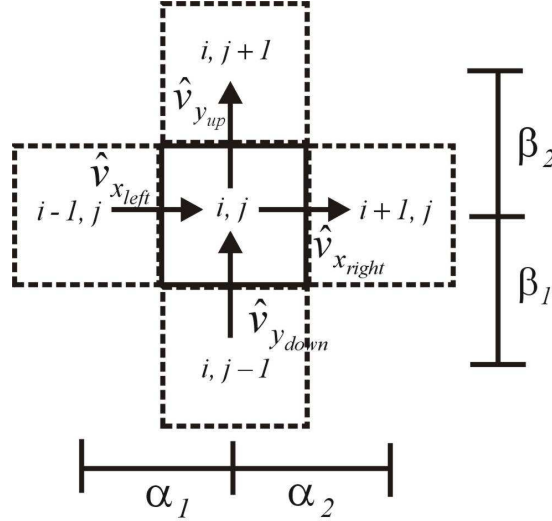


Figure B.1 – Pseudo-convective flux in the node i,j .

was obtained combining the finite volume method with the doner-cell upwind method to assure mass conservation. Height mass flux directions (Figure B.2) were adopted – Doner-Cell upwind method.

Pseudo-velocities, $\hat{v}_{x_{left}}$, $\hat{v}_{x_{right}}$, $\hat{v}_{y_{down}}$ and $\hat{v}_{y_{up}}$, are defined through the pseudo-velocities of nodes $(i-1, j)$, $(i, j-1)$, (i, j) , $(i+1, j)$, $(i, j+1)$ (Figure B.1):

$$\hat{v}_{x_{left}} = \frac{\hat{v}_{x_{i-1,j}} + \hat{v}_{x_{i,j}}}{2} \quad (\text{B.2})$$

$$\hat{v}_{x_{right}} = \frac{\hat{v}_{x_{i,j}} + \hat{v}_{x_{i+1,j}}}{2} \quad (\text{B.3})$$

$$\hat{v}_{y_{down}} = \frac{\hat{v}_{y_{i,j}} + \hat{v}_{y_{i,j-1}}}{2} \quad (\text{B.4})$$

$$\hat{v}_{y_{up}} = \frac{\hat{v}_{y_{i,j+1}} + \hat{v}_{y_{i,j}}}{2} \quad (\text{B.5})$$

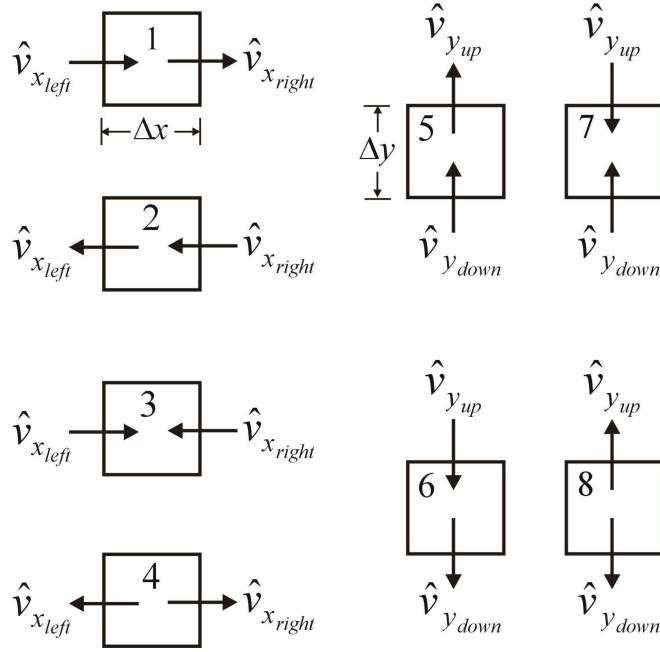


Figure B.2 – Doner-Cell upwind method.

As example, mass balance to case 1 (component x of pseudo-velocity) of Figure B.2 is discretized as:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = - \left(\frac{\hat{v}_{x_{right}} c_{i,j}^{k+1} - \hat{v}_{x_{left}} c_{i-1,j}^{k+1}}{\Delta x} \right) \quad (\text{B.6})$$

and mass balance to case 5 (component y of pseudo-velocity) of Figure B.2 as:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = - \left(\frac{\hat{v}_{y_{up}} c_{i,j}^{k+1} - \hat{v}_{y_{down}} c_{i,j-1}^{k+1}}{\Delta y} \right) \quad (\text{B.7})$$

where $c_{i,j}^k$ represents the normalized concentration in the control volume i,j at a current iteration k , Δt represents the time step, and Δx and Δy (Figure B.2) are defined, respectively, by:

$$\Delta x = \frac{\alpha_1 + \alpha_2}{2} \quad (\text{B.8})$$

$$\Delta y = \frac{\beta_1 + \beta_2}{2} \quad (\text{B.9})$$

where α_1 , α_2 , β_1 and β_2 (Figure B.1) are:

$$\alpha_1 = x_{i,j} - x_{i-1,j} \quad (\text{B.10})$$

$$\alpha_2 = x_{i+1,j} - x_{i,j} \quad (\text{B.11})$$

$$\beta_1 = y_{i,j} - y_{i,j-1} \quad (\text{B.12})$$

$$\beta_2 = y_{i,j+1} - y_{i,j} \quad (\text{B.13})$$

✓ **Coefficients of discretized equations (pseudo-convective flux):**

The discretization (in horizontal and vertical directions) of the mass transport equations with pseudo-convective terms were obtained and implemented in the numerical code:

$$k_d \Delta t c_{i-1,j}^{k+1} + (k_{c1} \Delta t + k_{c2} \Delta t - 1) c_{i,j}^{k+1} + k_b \Delta t c_{i+1,j}^{k+1} = -c_{i,j}^k \quad (\text{B.14})$$

$$k_d \Delta t c_{i,j-1}^{k+1} + (k_{c3} \Delta t + k_{c4} \Delta t - 1) c_{i,j}^{k+1} + k_e \Delta t c_{i,j+1}^{k+1} = -c_{i,j}^k \quad (\text{B.15})$$

Coefficients of equations (B.14) and (B.15), for each case of Figure 1, are presented in Table B.1 and Table B.2, respectively:

Table B.1 – Coefficients of equation (B.14) (case 1 to 4 of Figure B.2).

Pseudo-velocity directions - component x (Figure B.2)	k_a	k_b	k_{c1}	k_{c2}
1) $(\hat{v}_{x_{left}} > 0) \wedge (\hat{v}_{x_{right}} > 0)$	$2 \frac{\hat{v}_{x_{left}}}{\alpha_1 + \alpha_2}$	0	$-2 \frac{\hat{v}_{x_{right}}}{\alpha_1 + \alpha_2}$	0
2) $(\hat{v}_{x_{left}} < 0) \wedge (\hat{v}_{x_{right}} < 0)$	0	$-2 \frac{\hat{v}_{x_{right}}}{\alpha_1 + \alpha_2}$	0	$2 \frac{\hat{v}_{x_{left}}}{\alpha_1 + \alpha_2}$
3) $(\hat{v}_{x_{left}} > 0) \wedge (\hat{v}_{x_{right}} < 0)$	$2 \frac{\hat{v}_{x_{left}}}{\alpha_1 + \alpha_2}$	$-2 \frac{\hat{v}_{x_{right}}}{\alpha_1 + \alpha_2}$	0	0
4) $(\hat{v}_{x_{left}} < 0) \wedge (\hat{v}_{x_{right}} > 0)$	0	0	$-2 \frac{\hat{v}_{x_{right}}}{\alpha_1 + \alpha_2}$	$2 \frac{\hat{v}_{x_{left}}}{\alpha_1 + \alpha_2}$

Table B.2 – Coefficients of equation (B.15) (case 5 to 8 of Figure B.2).

Pseudo-velocity directions – component y (Figure B.2)	k_{c3}	k_{c4}	k_d	k_e
5) $(\hat{v}_{y_{up}} > 0) \wedge (\hat{v}_{y_{down}} > 0)$	$-2 \frac{\hat{v}_{y_{up}}}{\beta_1 + \beta_2}$	0	$2 \frac{\hat{v}_{y_{down}}}{\beta_1 + \beta_2}$	0
6) $(\hat{v}_{y_{up}} < 0) \wedge (\hat{v}_{y_{down}} < 0)$	0	$2 \frac{\hat{v}_{y_{down}}}{\beta_1 \beta_2}$	0	$-2 \frac{\hat{v}_{y_{up}}}{\beta_1 \beta_2}$
7) $(\hat{v}_{y_{up}} < 0) \wedge (\hat{v}_{y_{down}} > 0)$	0	0	$2 \frac{\hat{v}_{y_{down}}}{\beta_1 \beta_2}$	$-2 \frac{\hat{v}_{y_{up}}}{\beta_1 \beta_2}$
8) $(\hat{v}_{y_{up}} > 0) \wedge (\hat{v}_{y_{down}} < 0)$	$-2 \frac{\hat{v}_{y_{up}}}{\beta_1 \beta_2}$	$2 \frac{\hat{v}_{y_{down}}}{\beta_1 \beta_2}$	0	0

✓ **Discretized boundary conditions (pseudo-convective flux):**

Boundary conditions, of mass transport equation with pseudo-convective terms, at the membrane surface and at the symmetric axis were incorporated in the numerical resolution of the discretized equations. Pseudo-velocities for these boundaries are different from those cited previously.

At **membrane surface**, the pseudo-velocity down is defined as:

$$- \hat{v}_{y_{down}} = 0 \quad (B.16)$$

when membrane is impermeable to the solute;

$$- \hat{v}_{y_{down}} = \hat{v}_{y_{i,j}} (1 - R_{i,j}) \quad (B.17)$$

when the membrane is partially permeable to the solute ($R_{i,j}$ is the rejection coefficient of the solute relatively to the membrane);

$$- \hat{v}_{y_{down}} = \hat{v}_{y_{i,j}} \quad (B.18)$$

when the membrane is fully permeable to the solutes.

At **symmetric axis**, the pseudo-velocity up is equal to zero:

$$\hat{v}_{y_{up}} = 0 \quad (B.19)$$

At the cell inlet and outlet, it was not necessary to define boundary conditions incorporated in the discretization resolution. So that, at the **cell inlet**, the normalized concentration of the solute is equal to 1:

$$c = 1 \quad (B.20)$$

and, at the **cell outlet**, the variation of the normalized concentration is equal to zero:

$$\frac{\partial c}{\partial x} = 0 \quad (B.21)$$

B.2. Discretization method of mass transport equation with diffusive terms

✓ Mass transport equation with diffusive terms:

$$\frac{\partial c}{\partial t} = \frac{1}{Pe} \frac{\partial^2 c}{\partial x^2} + \frac{1}{Pe} \frac{\partial^2 c}{\partial y^2} \quad (\text{B.22})$$

✓ Mass balance (diffusive flux):

Mass balance to the discretized node of Figure B.3:

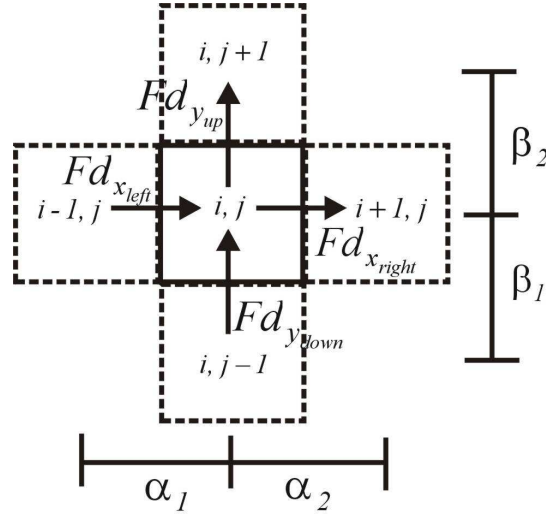


Figure B.3 – Diffusive mass flux in the node i,j .

was obtained for the longitudinal and normal directions through the finite volume method:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = \frac{Fd_{x_{left}}}{\Delta x} - \frac{Fd_{x_{right}}}{\Delta x} \quad (\text{B.23})$$

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = \frac{Fd_{y_{down}}}{\Delta y} - \frac{Fd_{y_{up}}}{\Delta y} \quad (\text{B.24})$$

where $c_{i,j}^k$ represents the normalized concentration in the control volume i,j and at a current iteration k and Δt represents the time step. The diffusive mass fluxes at the inlet and outlet of the control volume (Figure B.3) are defined by:

$$Fd_{x_{left}} = -\frac{1}{Pe} \frac{c_{i,j}^{k+1} - c_{i-1,j}^{k+1}}{x_{i,j} - x_{i-1,j}} \quad (B.25)$$

$$Fd_{x_{right}} = -\frac{1}{Pe} \frac{c_{i,j}^{k+1} - c_{i+1,j}^{k+1}}{x_{i+1,j} - x_{i,j}} \quad (B.26)$$

$$Fd_{y_{down}} = -\frac{1}{Pe} \frac{c_{i,j}^{k+1} - c_{i,j-1}^{k+1}}{y_{i,j} - y_{i,j-1}} \quad (B.27)$$

$$Fd_{y_{up}} = -\frac{1}{Pe} \frac{c_{i,j}^{k+1} - c_{i,j+1}^{k+1}}{y_{i,j+1} - y_{i,j}} \quad (B.28)$$

Δx and Δy are defined, respectively, by equation (B.8) and (B.9) and α_1 , α_2 , β_1 and β_2 (Figure B.3) by equations (B.10), (B.11), (B.12) and (B.13).

✓ **Coefficients of discretized equations (diffusive flux):**

From all theses equations, discretized mass balance equations with diffusive terms were obtained and implemented in the numerical code:

$$k_a \Delta t c_{i-1,j}^{k+1} + (k_{c1} \Delta t - 1) c_{i,j}^{k+1} + k_b \Delta t c_{i+1,j}^{k+1} = -c_{i,j}^k \quad (B.29)$$

$$k_d \Delta t c_{i,j-1}^{k+1} + (k_{c2} \Delta t - 1) c_{i,j}^{k+1} + k_e \Delta t c_{i,j+1}^{k+1} = -c_{i,j}^k \quad (B.30)$$

where the coefficients of equations (B.29) and (B.30) are:

$$k_a = 2 \frac{\alpha_2}{Pe \alpha_1 \alpha_2 (\alpha_1 + \alpha_2)} \quad (B.31)$$

$$k_b = 2 \frac{\alpha_1}{\text{Pe} \alpha_1 \alpha_2 (\alpha_1 + \alpha_2)} \quad (\text{B.32})$$

$$k_{c1} = -2 \frac{(\alpha_1 + \alpha_2)}{\text{Pe} \alpha_1 \alpha_2 (\alpha_1 + \alpha_2)} \quad (\text{B.33})$$

$$k_{c2} = -2 \frac{(\beta_1 + \beta_2)}{\text{Pe} \beta_1 \beta_2 (\beta_1 + \beta_2)} \quad (\text{B.34})$$

$$k_d = 2 \frac{\beta_2}{\text{Pe} \beta_1 \beta_2 (\beta_1 + \beta_2)} \quad (\text{B.35})$$

$$k_e = 2 \frac{\beta_1}{\text{Pe} \beta_1 \beta_2 (\beta_1 + \beta_2)} \quad (\text{B.36})$$

✓ **Discretized boundary conditions (diffusive flux):**

Boundary conditions, of mass transport equation with diffusive terms, at the cell inlet, cell outlet, membrane surface and symmetric axis were incorporated in the discretization resolution of the mass transport equation with diffusive terms. A diffusive mass balance was performed for each specific boundary.

At the **cell inlet**, the diffusive mass balance is:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = - \frac{F d_{x_{right}}}{\Delta x} \quad (\text{B.37})$$

In the lateral boundaries, control volume of node i,j has half of the length of Figure B.3:

$$\Delta x = \frac{\alpha_2}{2} \quad (\text{B.38})$$

The discretized equation for this boundary is:

$$(k_{c1} \Delta t - 1) c_{i,j}^{k+1} + k_b \Delta t c_{i+1,j}^{k+1} = -c_{i,j}^k \quad (\text{B.39})$$

and the respective coefficients are:

$$k_b = \frac{2}{\text{Pe}\alpha_2\alpha_2} \quad (\text{B.40})$$

$$k_{c1} = -\frac{2}{\text{Pe}\alpha_2\alpha_2} \quad (\text{B.41})$$

At the **cell outlet**, the diffusive mass balance is:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = \frac{Fd_{x_{\text{left}}}}{\Delta x} \quad (\text{B.42})$$

where

$$\Delta x = \frac{\alpha_1}{2} \quad (\text{B.43})$$

The discretized equation for this boundary is:

$$k_a \Delta t c_{i-1,j}^{k+1} + (k_{c1} \Delta t - 1) c_{i,j}^{k+1} = -c_{i,j}^k \quad (\text{B.44})$$

and the coefficients are:

$$k_a = \frac{2}{\text{Pe}\alpha_1\alpha_1} \quad (\text{B.45})$$

$$k_{c1} = -\frac{2}{\text{Pe}\alpha_1\alpha_1} \quad (\text{B.46})$$

At the **membrane surface**, the diffusive mass balance is reported by:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = -\frac{Fd_{y_{\text{up}}}}{\Delta y} \quad (\text{B.47})$$

where, in the top-bottom boundaries, control volume of node i,j has half of the height of Figure B.3:

$$\Delta y = \frac{\beta_2}{2} \quad (\text{B.48})$$

The discretized equation for this boundary is:

$$(k_{c2}\Delta t - 1)c_{i,j}^{k+1} + k_e\Delta tc_{i,j+1}^{k+1} = -c_{i,j}^k \quad (\text{B.49})$$

and the respective coefficients are:

$$k_{c2} = -\frac{2}{\text{Pe}\beta_2\beta_2} \quad (\text{B.50})$$

$$k_e = \frac{2}{\text{Pe}\beta_2\beta_2} \quad (\text{B.51})$$

At the **symmetric axis**, the diffusive mass balance is:

$$\frac{c_{i,j}^{k+1} - c_{i,j}^k}{\Delta t} = \frac{Fd_{y_{down}}}{\Delta y} \quad (\text{B.52})$$

where

$$\Delta y = \frac{\beta_1}{2} \quad (\text{B.53})$$

The discretized equation for this boundary is:

$$k_d\Delta tc_{i,j-1}^{k+1} + (k_{c2}\Delta t - 1)c_{i,j}^{k+1} = -c_{i,j}^k \quad (\text{B.54})$$

and the coefficients are:

$$k_{c2} = -\frac{2}{\text{Pe}\beta_1\beta_1} \quad (\text{B.55})$$

$$k_d = \frac{2}{\text{Pe}\beta_1\beta_1} \quad (\text{B.56})$$

B.3. Nomenclature

c	Normalized concentration
$c_{i,j}^k$	Normalized concentration of a discretized node i,j and at a current iteration k
$Fd_{x_{left}}$	Diffusive mass flux in the horizontal direction and on the left of the discretized node
$Fd_{x_{right}}$	Diffusive mass flux in the horizontal direction and on the right of the discretized node
$Fd_{y_{down}}$	Diffusive mass flux in the vertical direction and down the discretized node
$Fd_{y_{up}}$	Diffusive mass flux in the vertical direction and up the discretized node
k	Iteration k
k_a	Coefficient of discretized equation
k_b	Coefficient of discretized equation
k_{c1}	Coefficient of discretized equation
k_{c2}	Coefficient of discretized equation
k_{c3}	Coefficient of discretized equation
k_{c4}	Coefficient of discretized equation
k_d	Coefficient of discretized equation
k_e	Coefficient of discretized equation
$R_{i,j}$	Rejection coefficient of a component in a discretized node i,j
t	Non-dimensional time
$\hat{v}_x$	Normalized pseudo-velocity (component x)
$\hat{v}_{x_{left}}$	Normalized pseudo-velocity in the horizontal direction and on the left of the discretized node
$\hat{v}_{x_{right}}$	Normalized pseudo-velocity in the horizontal direction and on the right of the discretized node
$\hat{v}_y$	Normalized pseudo-velocity (component y)
$\hat{v}_{y_{down}}$	Normalized pseudo-velocity in the vertical direction and down the discretized node

$\hat{v}_{y_{up}}$	Normalized pseudo-velocity in the vertical direction and up the discretized node
x	Normalized longitudinal coordinate
$x_{i,j}$	Normalized longitudinal coordinate of a discretized node i,j
y	Normalized vertical coordinate
$y_{i,j}$	Normalized vertical coordinate of a discretized node i,j

Non-dimensional numbers

Pe	Peclet number

Greek Symbols

α_1	Equation (B.10)
α_2	Equation (B.11)
β_1	Equation (B.12)
β_2	Equation (B.13)
Δt	Non-dimensional time step
Δx	Equation (B.8)
Δy	Equation (B.9)

Appendix C

Vorticity transport equation with electric terms

This Appendix shows the deduction of the vorticity transport equation with electric terms.

C.1. Deduction of the vorticity transport equation with electric terms

➤ Velocity component equations with electric terms

The momentum equations, with electric terms incorporated, along Cartesian Coordinates (x and y) are:

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -E\mu_0 \frac{\partial p}{\partial x} + \frac{1}{\text{Re}} \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right) - \Pi_1 r_e \frac{\partial \phi}{\partial x} \quad (\text{C.1})$$

$$\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} = -E\mu_0 \frac{\partial p}{\partial y} + \frac{1}{\text{Re}} \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right) - \Pi_1 r_e \frac{\partial \phi}{\partial y} \quad (\text{C.2})$$

These equations are composed by a time derivative term (at the left), convective terms, a pressure term, diffusive terms and a electric term (at the right).

✓ Convective terms of vorticity transport equation:

Deriving the convective terms, $v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y}$ and $v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y}$, in order to y and x , respectively, the terms become:

$$\frac{\partial}{\partial y} \left(v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} \right) = \frac{\partial v_x}{\partial y} \frac{\partial v_x}{\partial x} + v_x \frac{\partial^2 v_x}{\partial x \partial y} + \frac{\partial v_y}{\partial y} \frac{\partial v_x}{\partial y} + v_y \frac{\partial^2 v_x}{\partial y^2} \quad (\text{C.3})$$

$$\frac{\partial}{\partial x} \left(v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} \right) = \frac{\partial v_x}{\partial x} \frac{\partial v_y}{\partial x} + v_x \frac{\partial^2 v_y}{\partial x^2} + \frac{\partial v_y}{\partial x} \frac{\partial v_y}{\partial y} + v_y \frac{\partial^2 v_y}{\partial x \partial y} \quad (\text{C.4})$$

Then, subtracting equation (C.3) to equation (C.4), the result is the following:

$$\frac{\partial v_x}{\partial y} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) - \frac{\partial v_y}{\partial x} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) + v_x \left(\frac{\partial^2 v_x}{\partial x \partial y} - \frac{\partial^2 v_y}{\partial x^2} \right) + v_y \left(\frac{\partial^2 v_x}{\partial y^2} - \frac{\partial^2 v_y}{\partial x \partial y} \right) \quad (C.5)$$

Defining the secondary variable vorticity, ω , as:

$$\omega = \frac{\partial v_x}{\partial y} - \frac{\partial v_y}{\partial x} \quad (C.6)$$

and deriving this variable in order to x and y :

$$\frac{\partial \omega}{\partial x} = \frac{\partial^2 v_x}{\partial y \partial x} - \frac{\partial^2 v_y}{\partial x^2} \quad (C.7)$$

$$\frac{\partial \omega}{\partial y} = \frac{\partial^2 v_x}{\partial y^2} - \frac{\partial^2 v_y}{\partial x \partial y} \quad (C.8)$$

Combining the previous equations and considering mass conservation,

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (C.9)$$

equation (C.5) becomes simplified:

$$\frac{\partial v_x}{\partial y} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) - \frac{\partial v_y}{\partial x} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) + v_x \left(\frac{\partial^2 v_x}{\partial x \partial y} - \frac{\partial^2 v_y}{\partial x^2} \right) + v_y \left(\frac{\partial^2 v_x}{\partial y^2} - \frac{\partial^2 v_y}{\partial x \partial y} \right) = v_x \frac{\partial \omega}{\partial x} + v_y \frac{\partial \omega}{\partial y} \quad (C.10)$$

✓ **Diffusive terms of vorticity transport equation:**

Another similar procedure was followed for the diffusive terms, $\frac{1}{\text{Re}} \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right)$ and

$\frac{1}{\text{Re}} \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right)$, of the momentum equations. These terms were, also, derived in order to

y and x , respectively:

$$\frac{\partial}{\partial y} \left[\frac{1}{\text{Re}} \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right) \right] = \frac{1}{\text{Re}} \frac{\partial^3 v_x}{\partial x^2 \partial y} + \frac{1}{\text{Re}} \frac{\partial^3 v_x}{\partial y^3} \quad (\text{C.11})$$

$$\frac{\partial}{\partial x} \left[\frac{1}{\text{Re}} \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right) \right] = \frac{1}{\text{Re}} \frac{\partial^3 v_y}{\partial x^3} + \frac{1}{\text{Re}} \frac{\partial^3 v_y}{\partial y^2 \partial x} \quad (\text{C.12})$$

Subtracting equation (C.11) to equation (C.12), the following term was obtained:

$$\frac{1}{\text{Re}} \left[\left(\frac{\partial^3 v_x}{\partial x^2 \partial y} - \frac{\partial^3 v_y}{\partial x^3} \right) + \left(\frac{\partial^3 v_x}{\partial y^3} - \frac{\partial^3 v_y}{\partial x \partial y^2} \right) \right] \quad (\text{C.13})$$

Then, deriving equations (C.7) and (C.8), the derivatives of second order of equation (C.6) are:

$$\frac{\partial^2 \omega}{\partial x^2} = \frac{\partial^3 v_x}{\partial y \partial x^2} - \frac{\partial^3 v_y}{\partial x^3} \quad (\text{C.14})$$

$$\frac{\partial^2 \omega}{\partial y^2} = \frac{\partial^3 v_x}{\partial y^3} - \frac{\partial^3 v_y}{\partial x \partial y^2} \quad (\text{C.15})$$

According to previous equations and considering the continuity equation, equation (C.13) becomes:

$$\frac{1}{\text{Re}} \left[\left(\frac{\partial^3 v_x}{\partial x^2 \partial y} - \frac{\partial^3 v_y}{\partial x^3} \right) + \left(\frac{\partial^3 v_x}{\partial y^3} - \frac{\partial^3 v_y}{\partial x \partial y^2} \right) \right] = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) \quad (\text{C.16})$$

✓ **Electric terms of vorticity transport equation:**

Electric terms of the velocity equations, $-\Pi_1 r_e \frac{\partial \phi}{\partial x}$ and $-\Pi_1 r_e \frac{\partial \phi}{\partial y}$, were derived, in order to y and x, respectively.

$$\frac{\partial}{\partial y} \left(-\Pi_1 r_e \frac{\partial \phi}{\partial x} \right) = -\Pi_1 \frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \Pi_1 r_e \frac{\partial^2 \phi}{\partial x \partial y} \quad (\text{C.17})$$

$$\frac{\partial}{\partial x} \left(-\Pi_1 r_e \frac{\partial \phi}{\partial y} \right) = -\Pi_1 \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} - \Pi_1 r_e \frac{\partial^2 \phi}{\partial x \partial y} \quad (\text{C.18})$$

Subtracting equation (C.17) from equation (C.18), the electric term of the vorticity transport equation becomes:

$$-\Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) \quad (\text{C.19})$$

✓ **Time derivative term of vorticity transport equation:**

The terms, $\frac{\partial v_x}{\partial t}$ and $\frac{\partial v_y}{\partial t}$, of the momentum equations, were also derived in order to y and x, respectively:

$$\frac{\partial}{\partial y} \left(\frac{\partial v_x}{\partial t} \right) = \frac{\partial}{\partial t} \left(\frac{\partial v_x}{\partial y} \right) \quad (\text{C.20})$$

$$\frac{\partial}{\partial x} \left(\frac{\partial v_y}{\partial t} \right) = \frac{\partial}{\partial t} \left(\frac{\partial v_y}{\partial x} \right) \quad (\text{C.21})$$

Then, subtracting equation (C.20) from equation (C.21), the derivative of the vorticity variable in order to time is:

$$\frac{\partial}{\partial t} \left(\frac{\partial v_x}{\partial y} - \frac{\partial v_y}{\partial x} \right) = \frac{\partial \omega}{\partial t} \quad (\text{C.22})$$

✓ **Pressure term of the vorticity transport equation:**

Furthermore, the pressure terms of the velocity equations, $-E\mu_0 \frac{\partial p}{\partial x}$ and $-E\mu_0 \frac{\partial p}{\partial y}$, were derived in order to y and x:

$$\frac{\partial}{\partial y} \left(-E\mu_0 \frac{\partial p}{\partial x} \right) = -E\mu_0 \frac{\partial^2 p}{\partial x \partial y} \quad (\text{C.23})$$

$$\frac{\partial}{\partial x} \left(-E\mu_0 \frac{\partial p}{\partial y} \right) = -E\mu_0 \frac{\partial^2 p}{\partial x \partial y} \quad (\text{C.24})$$

Then, subtracting equation (C.23) from equation (C.24), the pressure terms of the vorticity transport equation cancel:

$$-E\mu_0 \frac{\partial^2 p}{\partial x \partial y} + E\mu_0 \frac{\partial^2 p}{\partial x \partial y} = 0 \quad (\text{C.25})$$

➤ Vorticity transport equation with electric terms

After deriving the momentum component equations, in order to x and y , and subtracting both equations, the vorticity transport equation with the electric terms is:

$$\frac{\partial \omega}{\partial t} + v_x \frac{\partial \omega}{\partial x} + v_y \frac{\partial \omega}{\partial y} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) - \Pi_1 \left(\frac{\partial r_e}{\partial y} \frac{\partial \phi}{\partial x} - \frac{\partial r_e}{\partial x} \frac{\partial \phi}{\partial y} \right) \quad (\text{C.26})$$

The convective, diffusive and independent (electric) terms of the vorticity transport equation (C.26) were discretized by a finite differences method. An implicit method was used in the discretization of all the terms and an upwind technique in the discretization of the convective terms. This equation was used in Chapter 7 and 8.

✓ Vorticity transport equation considering simplified Poisson-Boltzmann equation

In case of the simplified Poisson-Boltzmann equation (in Chapter 6), the sum of the ionic concentrations, r_e , is:

$$r_e = 2\Pi_3(\phi - \phi_0) \text{ where } \phi_0 = 0 \quad (\text{C.27})$$

and the momentum equations are:

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -E\mu_0 \frac{\partial p}{\partial x} + \frac{1}{\text{Re}} \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right) - 2\Pi_1\Pi_3\phi \frac{\partial \phi}{\partial x} \quad (\text{C.28})$$

$$\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} = -E\mu_0 \frac{\partial p}{\partial y} + \frac{1}{\text{Re}} \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right) - 2\Pi_1\Pi_3\phi \frac{\partial \phi}{\partial y} \quad (\text{C.29})$$

Deriving the electric terms, $2\Pi_1\Pi_3\phi \frac{\partial \phi}{\partial x}$ and $2\Pi_1\Pi_3\phi \frac{\partial \phi}{\partial y}$, of the momentum equations (C.28) and (C.29), in order to y and x , respectively, becomes:

$$\frac{\partial}{\partial y} \left(2\Pi_1\Pi_3\phi \frac{\partial \phi}{\partial x} \right) = 2\Pi_1\Pi_3 \left(\frac{\partial \phi}{\partial y} \frac{\partial \phi}{\partial x} + \phi \frac{\partial^2 \phi}{\partial x \partial y} \right) \quad (\text{C.30})$$

$$\frac{\partial}{\partial x} \left(2\Pi_1\Pi_3\phi \frac{\partial \phi}{\partial y} \right) = 2\Pi_1\Pi_3 \left(\frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} + \phi \frac{\partial^2 \phi}{\partial x \partial y} \right) \quad (\text{C.31})$$

Subtracting equation (C.30) from equation (C.31), the electric term of the vorticity transport equation is null, i.e.:

$$2\Pi_1\Pi_3 \left(\frac{\partial \phi}{\partial y} \frac{\partial \phi}{\partial x} + \phi \frac{\partial^2 \phi}{\partial x \partial y} \right) - 2\Pi_1\Pi_3 \left(\frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} + \phi \frac{\partial^2 \phi}{\partial x \partial y} \right) = 0 \quad (\text{C.32})$$

The vorticity transport equation becomes:

$$\frac{\partial \omega}{\partial t} + v_x \frac{\partial \omega}{\partial x} + v_y \frac{\partial \omega}{\partial y} = \frac{1}{\text{Re}} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) \quad (\text{C.33})$$

Vorticity equation (C.33) was used in Chapter 6.

C.2. Nomenclature

C_{ref}^0 Concentration of the reference component at the feed/bulk

F	Faraday constant
M_{ref}	Molar mass of the reference component
p	Normalized pressure
R	Gas constant
r_e	Sum of the normalized ionic concentrations
T	Temperature
t	Non-dimensional time
V_0	Mean feed velocity
v_x	Normalized longitudinal component of the velocity
v_y	Normalized vertical component of the velocity
x	Normalized longitudinal coordinate
y	Normalized vertical coordinate

Non-dimensional numbers

Re	Reynolds number of the solution
Π_1	$\Pi_1 = \frac{FC_{ref}^0 \Phi_w}{M_{ref} \rho V_0^2}$
Π_3	$\Pi_3 = \frac{F\Phi_w}{RT}$

Greek Symbols

$E\mu_0$	Euler number
ρ	Density
ω	Vorticity
Φ_w	Membrane electric potential
ϕ	Normalized electric potential
ϕ_0	Normalized electric potential of the bulk