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Grau en
Enginyeria
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Treball Final de Grau

Numerical solution of transport phenomena equations for nanofiltration membranes.

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June, 2019

UNIVERSITAT DE
BARCELONA

"Cal tenir la ment oberta.

Però no tant com perquè se't caigui el cervell".

Richard Feynman

En primer lloc agrair de tot cor als meus pares per tot l'amor i esforç en tots aquests anys, sense ells no hauria estat possible. Agrair especialment a la Julia, pel seu suport incondicional durant tots aquests anys.

Agrair al Dr. Llorens i al Dr. Mas per tot el seu suport i consells durant tot aquest projecte i sobretot per ser grans professors i persones.

Per acabar agrair a tots els amics de classe i a tots els professors de la UB per fer d'aquesta etapa inoblidable.

Contents

SUMMARY

Nanofiltration is a membrane separation process whose driving force are pressure changes, which is used to remove ionic species from aqueous solutions. This technique lies between reverse osmosis and ultrafiltration membranes. Nanofiltration has received much attention in the last decades due to its applications in textile, paper, and food industries including water desalination.

The separation mechanisms of nanofiltration membranes include steric and electric effects. Most of these membranes acquire an electrical charge when they come into contact with a polar medium due to the adsorption of charged species from the bulk to the pore walls, which leads to the favored transport of counter-ions and the exclusion of co-ions.

The development of adequate mathematical models for nanofiltration is extremely important for better understanding of electrolyte transport phenomena and prediction of separation parameters. The transport of ions in charged membrane pores can be described by the system of Nernst–Planck, Poisson, and Navier–Stokes equations.

In this work is modeled the behavior of ions, in our case NaCl, through a nanofiltration membrane with the system of differential equations of Nernst-Planck and Poisson in 1-D in transient. The system of partial differential equations is solved by means of numerical algorithms with the Wolfram Mathematica program. The results are compared with a more complex model (Poisson, Nernst-Planck and Navier Stokes in 2D) and a simpler model (Donnan-Steric-Partition-Dielectric exclusion model) to verify our work and later to be able to use the algorithm for more complex ionic systems.

Keywords: Nanofiltration, Membrane Transport Phenomena, Electro diffusion, Numerical modelling, Wolfram Mathematica.

RESUM

La nanofiltració és un procés de separació de membranes, la seva força motriu són els canvis de pressió, que s'utilitzen per eliminar espècies iòniques a partir de solucions aquoses. Aquesta tècnica es troba entre les membranes d'osmosi inversa i d'ultrafiltració. La nanofiltració ha rebut molta atenció en les últimes dècades a causa de les seves aplicacions en indústries tèxtils, papereres i alimentàries, incloent la dessalinització de l'aigua.

Els mecanismes de separació de les membranes de nanofiltració inclouen efectes estèrics i elèctrics. La majoria d'aquestes membranes adquireixen una càrrega elèctrica quan entren en contacte amb un medi polar provocant l'adsorció d'espècies carregades de la solució a les parets de la membrana, el que condueix al transport de contra-ions i l'exclusió de co-ions.

El desenvolupament de models matemàtics adequats per a la nanofiltració és extremadament important per a una millor comprensió dels fenòmens del transport electrolític i la predicció dels paràmetres de separació. El transport d'ions en membranes es descriu pel sistema de les equacions de Nernst – Planck, Poisson i Navier – Stokes.

En aquest treball s'ha modelat el comportament d'ions, en el nostre cas NaCl, a través d'una membrana de nanofiltració amb el sistema d'equacions diferencials de Nernst-Planck i Poisson en 1-D en no estacionari. El sistema d'equacions diferencials parcials s'ha resolt mitjançant algorismes numèrics amb el programa Wolfram Mathematica. Posteriorment s'han comparat els resultats amb un model més complex (Poisson, Nernst-Planck i Navier Stokes en 2D) i un model més senzill (model Donnan-Steric-Partition-Dielectric exclusion) per verificar el nostre treball i, més endavant, poder utilitzar l'algorisme per a sistemes iònics més complexos.

Paraules clau: Nanofiltració, fenòmens de transport de membrana, electro difusió, modelització numèrica, Wolfram Mathematica.

1. INTRODUCTION

Membrane processes are relatively new technology with many expectations for the future, applicable to many separation processes. They can be driven by various driving forces such as pressure, temperature, and electric potential. Pressure-driven membrane processes such as reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) use pressure gradient across the membrane in order to transfer species. These types of membranes are very useful in the separation of salts from aqueous solutions, e.g., to produce potable water. The major disadvantage of RO membranes is that they need high pressures [1]. For example, the reverse osmosis plant that supplies water for the Spanish province of Almeria requires a full third of the province's electricity [2].

Since RO membranes traditionally operate at high pressure and entail a high energy cost in the 1970s RO membranes operating at low pressure and with relatively high-water flows were investigated. These RO membranes at low pressure had great acceptance to be implemented as separation technology and have been called nanofiltration membranes [3]. The NF membranes are characterized by a pore diameter of a few nanometers, and an operating pressure between (7-30 bars). These operating characteristics place it between the RO membranes and the MF membranes [4]. As you can see in the following figure:
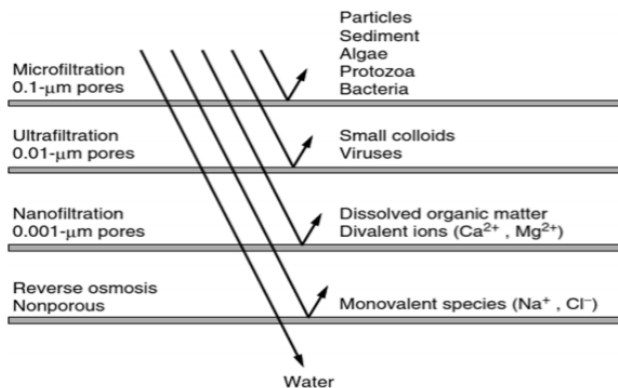

Figure 1. Differences in diameter of pores between pressure-driven membranes. (Crittenden et al. 2012)

Below can be seen a table with the main differences between the pressure membranes:

Membrane type	MF	UF	NF	RO
Porosity	porous	porous	finely porous	nonporous
Pore size (nm)	50-1,000	5-20	2-5	-
Membrane type	isotropic	asymmetric	asymmetric/ composite	asymmetric/ composite
Transfer mechanism	sieving, adsorption	sieving, preferential adsorption	sieving, electrostatic hydration, diffusion	diffusion
Driving force	pressure	pressure	pressure	pressure
Operating pressure (bar)	0.5-5	1-10	7-30	15-100

Figure 2. General characteristics of pressure-driven membranes. Sivonen et al. 2014

1.1. MEMBRANE CHARGE

The separation mechanisms of NF membranes include steric, dielectric and Donnan effects. Steric effect is caused by the ion size and the size of membrane pore, dielectric effects is caused by the difference of the dielectric constant between the bulk solution and the membrane domain, and Donnan effect is caused by the charge polarities of the ions and the surface charge of the membrane [5].

The membrane acquires electrical charge by three possible mechanisms [6]:

- Ionization of surface groups:
  - Dissociation of acidic groups on a membrane surface will give a negatively charged surface.
  - Dissociation of any basic groups on a membrane surface will give a positively charged surface.
  - The surface charge depends on the acidic or basic strengths of the surface groups and the ionic strength of the solution.

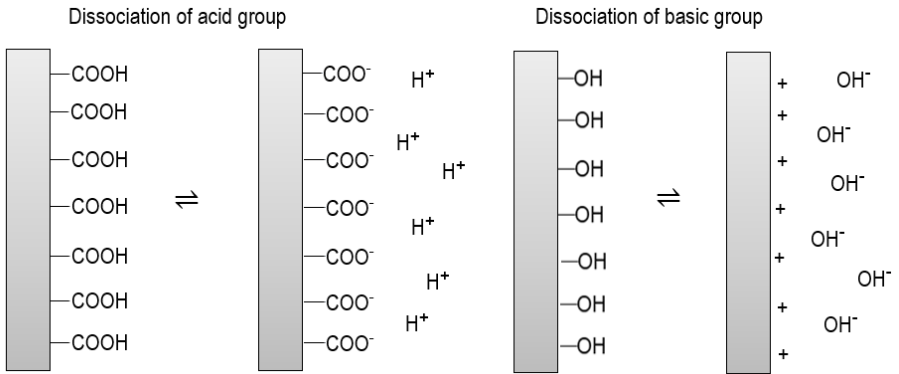Dissociation of acid group   Dissociation of basic group

Figure 3. Charged membrane by ionization of surface groups.

Differential loss of ions from the crystal lattice

- If a crystal of AgI is placed in water, it starts to dissolve.

- If equal amounts of Ag+ and I- ions were to dissolve, the surface would be electroneutral.

- Ag+ ions dissolve preferentially leaving a negatively charged surface.
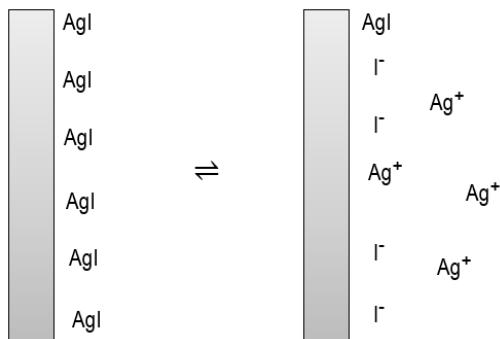

Figure 4. Charged membrane by the dissolve of preferentially ions.

- Adsorption of charged species

  - Surfactant ions may be specifically adsorbed onto the surface of a particle.

  - Cationic surfactants would lead to a positively charged surface.

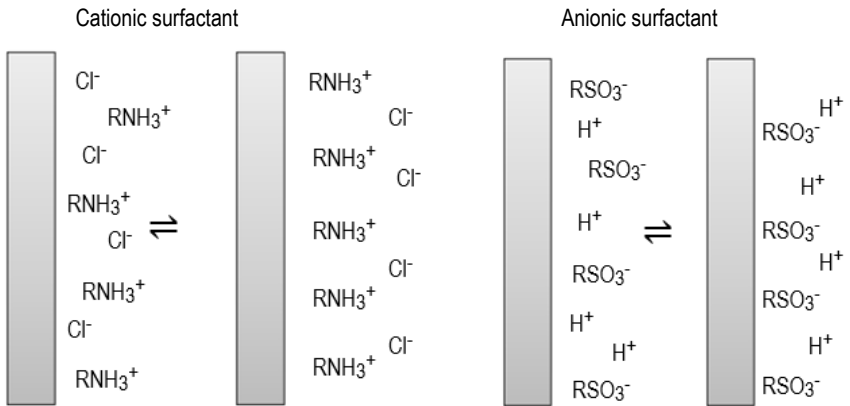 - Anionic surfactants would lead to a negatively charged surface.

Figure 5. Charged membrane by the adsorption of charged species.

1.2. ELECTRICAL DOUBLE LAYER MODELS

The electrical behaviour of a charged particle in an electrolyte solution depend strongly on the distribution of electrolyte ions and on the electric potential around the particle. In electrostatics the potential distribution is usually described by the Poisson-Boltzmann equation.

Poisson-Boltzmann assumes:

i.   Electrolyte ions are point charges

ii. Ion-ion correlation is neglected

iii. Solvent is a continuum dielectric with a uniform dielectric permittivity ε_r.

iv. Charges on the particle surface are smeared out to give a uniform surface charge density σ

A membrane in contact to an electrolyte is usually charged with adsorption of ions onto the membrane and/or ionization of dissociable groups on the surface explained in the last section.

Electrolytes with charges of the opposite sign are the counter ions and with the same sign are the co-ions.

They tend to approach the particle surface and to neutralize the surface charge, but thermal motion of these ions prevents accumulation of the ions so that around the membrane is formed an ionic cloud. In the ionic cloud the concentration of the counter ions become very high while that of co-ions become very low. The ionic cloud together with the surface charge forms an electrical double layer, often called electrical diffuse double layer [7].
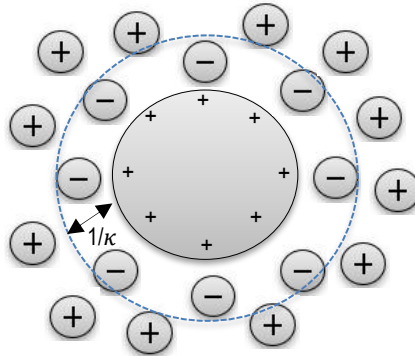

Figure 6. A positive particle surrounded by an electrical double layer of thickness $1/\kappa$

1.2.1   HELMHOLTZ-PERRIN MODEL

Created by Helmholtz in 1879, is the simplest model to describe interactions in surface charges. Suppose an electrode with a surface charge density σ_+ :
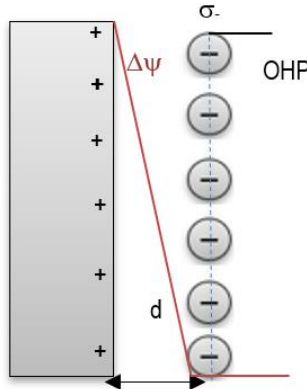
Figure 7. Schematic figure of Helmholtz-Perrin model

In the figure 7. can be seen that the charge on the electrode is balanced by the ions of the electrolyte solution with an equal but opposite amount of charge resulting two layers separated by a thickness d.

The boundary through the centre of the negative ions is called Outer Helmholtz Plane (OHP), this immobile layer was thought to completely neutralize the charge on the electrode [8]. Were the model of the electrical interface being precisely analogous to a parallel capacitor composed of two plates of opposite charge. The potential in the region d between the two parallel plates can be described by

$$E = \frac{\sigma}{\varepsilon_r \varepsilon_o} \tag{1}$$

$$E = -\frac{d\psi}{dx} = \frac{\sigma}{\varepsilon_r \varepsilon_o}\, d \tag{2}$$

Where E is the electrical field, σ the surface charge density, $\varepsilon_r \varepsilon_o$ the product with the permittivity of vacuum and the permittivity of the region.

Where the capacitance per unit area of the system is

$$C = \frac{\varepsilon_r \varepsilon_o}{d} \tag{3}$$

The potential results the classical solution of a parallel capacitor

$$\Delta\psi = \frac{\sigma\,A}{C} \tag{4}$$

Where A is the surface of the electrical layer.

Model limitation:

- $\Delta\psi$ decreases linearly with the distance to the surface
- $\Delta\psi$ does not account the concentration dependence
- $\Delta\psi \neq f(I) \equiv$ Ionic strength
- $\Delta\psi \neq f(T)$, does not account the thermal motion of the ions

1.2.2   GOUY CHAPMAN MODEL

Gouy and Chapman suggested that the capacitor parallel plate layer of Helmholtz model be replaced by a diffuse cloud of charge that was more concentrated near the electrode surface and extended out into the bulk solution [9]. The principle of the Gouy Chapman model assumes Local equilibrium hypotheses (LEH) that is a simplification of the non-equilibrium thermodynamics. LEH assumes that the variables of the system are varying in space and time but assumes that each small volume element of the system is well mixed (the variables changes very slowly and can be assumed that are constant in the volume element).

LEH can be described by the Boltzmann distribution based on the mean field theory having the assumptions in the 1.2 section.
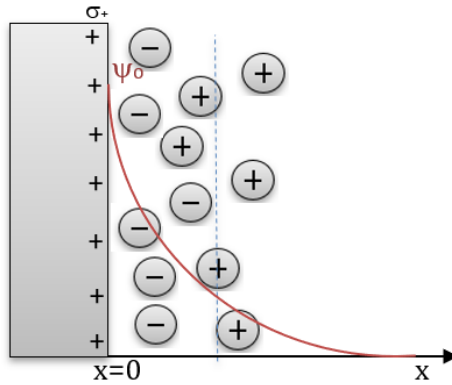
Figure 8. Schematic figure of Gouy-Chapman model

LEH can be described by the Boltzmann distribution based on the mean field theory that assumes the ions interacts with the charged surface through a mean potential generated by all ions in solution and all the surface charges, this assumption allows to describe all the ions as a continuum domain.

The electric field generated by a charge distribution can be described by the Poisson equation

$$-\nabla . (\varepsilon \, \nabla \, \psi) = \sum_{i}^{N} \rho_i \tag{5}$$

Where ε is the electric permittivity of the double layer and the ρ_i is the charge density. The charge density can be described as the sum of charges density of ions

$$\sum_{i}^{N} \rho_i = \sum_{i}^{N} z_i F \, c_i \tag{6}$$

Where z_i is the valence of the ion, F the Faraday's constant and c_i the ion concentration.

And the boundary conditions of the System

$$\left(\frac{d\psi}{dx}\right)_{x=0} = -\frac{\sigma}{\varepsilon} \tag{7}$$

$$\psi(x \to \infty) = 0 \tag{8}$$

The Boltzmann distribution in molar units has the form

$$c_i = c_{i,\infty} e^{-z_i F \psi / R T} \tag{9}$$

Where $c_{i,\infty}$ is the ion concentration of the bulk.

The Poisson-Boltzmann expressed in molar units can be expressed

$$-\nabla.(\varepsilon \, \nabla \, \psi) = \sum_i^N z_i F \, c_{i,\infty} e^{-z_i F \psi / R T} \tag{10}$$

Where $F = N_A e$

Solution of Poisson-Boltzmann allows us to find the potential distribution, and the concentration profiles of ions in solution.
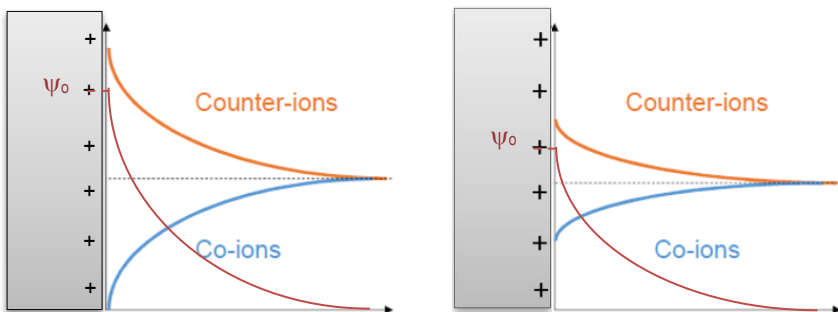

Figure 9. Concentration and potential profiles for different surface potential

1.2.2.1   LOW POTENTIAL APPROXIMATION

If the potential is low, in this case the thermal energy is bigger than the electrostatic interactions, this approach is called Debye-Hückel approximation. This approximation can be described as

$$z_i F \psi / R T \ll 1 \tag{11}$$

Where R is the universal gas constant of ideal gas.

Now the exponential term of the Poisson-Boltzmann equation can be expanded in series

$$e^{-z_i e \psi / R T} = 1 - z_i F \psi / R T + \frac{\left(z_i F \psi / R T\right)^2}{2!} - \dots \tag{12}$$

The series can be truncated at the first two terms, the Poisson Boltzmann equation can be rewritten as

$$-\nabla . (\varepsilon \nabla \psi) = \sum_i^N z_i F c_{i,\infty} \left(1 - z_i F \psi / R T\right) \tag{13}$$

The electroneutrality condition in the bulk electrolyte gives

$$\sum_i^N z_i F c_{i,\infty} = 0 \tag{14}$$

Inserting the electroneutrality condition in the P-B equation

$$-\nabla . (\nabla \psi) = \frac{1}{\varepsilon R T} \sum_i^N z_i^2 F^2 c_{i,\infty} \psi \tag{15}$$

Poisson-Boltzmann can be written in terms of the parameter

$$-\nabla \cdot (\varepsilon \, \nabla \, \psi) = \kappa^2 \psi \tag{16}$$

This equation is called the linearized Poisson Boltzmann equation, and the Debye-Hückel parameter can be defined as

$$\kappa^2 = \frac{1}{\varepsilon \, R \, T} \sum_i z_i^{\,2} F^2 \, c_{i,\infty} \tag{17}$$

If the ionic strength is defined the Debye-Hückel parameter can be rewritten as

$$I = \frac{1}{2} \sum_i^N z_i^{\,2} \, c_{i,\infty} \tag{18}$$

$$\kappa = \left(\frac{1}{\varepsilon \, R \, T} \sum_i^N z_i^{\,2} F^2 \, c_{i,\infty} \right)^{1/2} = \left(\frac{2 \, F^2 \, I}{\varepsilon \, R \, T} \right)^{1/2} = [m]^{-1} \tag{19}$$

The inverse of Debye-Hückel parameter κ^{-1} has units of length and is called the Debye length, having an important physical significance because represents the thickness of the electrical double layer. In the following graphics can be seen that if the ionic strength increases de Debye length decreases, this succeed because when the ionic strength increases the counter ions are more attracted to the interface and making the thickness of the double layer smaller.
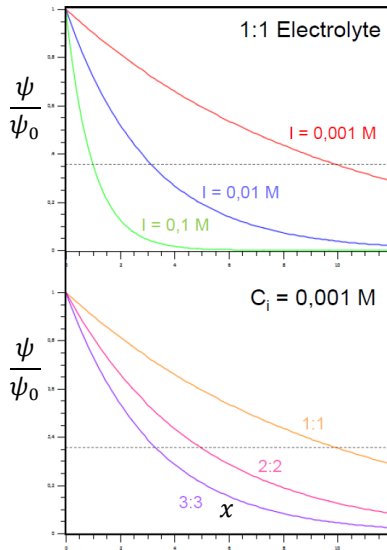
Figure 10. Electrical potential for different ionic strengths (a) and charge valence (b)

Gouy Chapman model limitations:

- Ion-ion interactions are not considered
- Ions are considered punctual
- Homogeneous distribution of surface charges
- It is not possible to consider adsorbed ions
- Constant permittivity in all the diffuse layer

1.2.3   STERN MODEL

Stern developed the double layer with a more realistic way for describe the interface. Stern model is a combination between the Helmholtz and Gouy Chapman model, describes the double layer by the compact layer of Helmholtz and next the diffuse layer of Gouy Chapman model. The model considers the ionic radius and the thickness of OHP layer depends of it.

Figure 11. Schematic figure of Stern model

1.3. **NERNST PLANCK EQUATIONS**

The last models based on Poisson-Boltzmann equation are correct to predict electrostatic phenomena, because they assume a Boltzmann distribution assuming they are in equilibrium. But in the case if membranes, not only the elect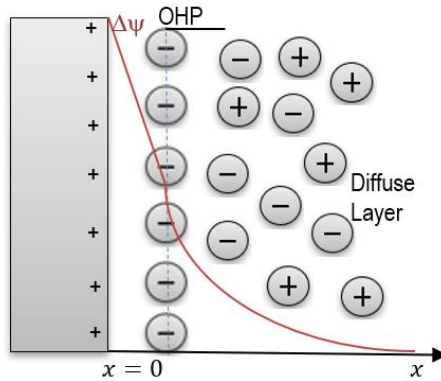rostatic interactions are included, the ions move by diffusion and by the fluid flow. In this case it is an electrodynamic phenomena, for predict these systems a more complex model is needed to be able to model it.

Considering a membrane in a confined region immersed in an electrolyte solution with a continuum dielectric permittivity and a continuum dielectric permittivity in the membrane.

Can be described by the system of equations of Poisson, Nernst-Planck and Navier-Stokes equations in 2-D.

The Nernst Planck (NP) equation is a conservation equation of mass species that describes the ionic concentration gradient influenced by an electric field. For deriving this equation, we can start with the conservation of mass equation for an incompressible fluid $(\nabla . u) = 0$:

$$\frac{\partial c_i}{\partial t} = u\nabla . c_i + \nabla . F_i \tag{20}$$

The convection term $(u\nabla. c_i)$ in dilute theory is easy to define, it is just the mass averaged velocity of the fluid, in this the velocity of the ions is the same as the fluid flow. But when the case is in concentrated solutions, this term become more difficult to define, because in this case we must distinct between the ion velocity and the solvent flow.

The flux for Nernst-Planck equations can be defined by:

$$F_i = -M_i c_i \vec{\nabla} \widetilde{\mu}_i \tag{21}$$

Where M_i is the mobility of the ion, defined by the Einstein relation

$$M_i = \frac{D_i}{K_b T} \tag{22}$$

c_i is the molar concentration of the ion and $\widetilde{\mu}_i$ is the electrochemical potential, the chemical potential is defined by the dilute theory as:

$$\mu_i = \left(\frac{\partial G}{\partial c_i} \right)_{T,P,c_{j\neq i}} = \mu_0 + RT \ ln \frac{c_i}{c_{i,0}} \tag{23}$$

Where $c_{i,0}$ is the concentration equal to 1M.

The electrochemical potential can be described adding de Coulombic force to the chemical potential

$$\widetilde{\mu}_i = \mu_0 + RT \ ln \frac{c_i}{c_{i,0}} + z_i F \ \psi \tag{24}$$

The gradient of the electrochemical potential is

$$\vec{\nabla} \widetilde{\mu}_i = \mu_i + z_i F \vec{\nabla} \psi = RT \ \vec{\nabla} \ ln \ c_i + z_i F \vec{\nabla} \psi \tag{24.a}$$

Where :

$$\vec{\nabla}\ ln\ c_i = \frac{\vec{\nabla}c_i}{c_i} \tag{25}$$

With this relationship gives:

$$\vec{\nabla}\widetilde{\mu}_i = RT\ \frac{\vec{\nabla}c_i}{c_i} + z_i F\ \vec{\nabla}\ \psi \tag{26}$$

With the Einstein relation and the chemical potential, the molar flux can be defined as

$$F_i = -M_i c_i \vec{\nabla}\widetilde{\mu}_i = -D_i \left(\vec{\nabla}c_i + \frac{z_i F}{RT}c_i\ \vec{\nabla}\ \psi\right) \tag{27}$$

This equation gives the flux due to the diffusion given by Fick's law and the second term is due to electromigration. With the continuity mass equation and the flux defined we can write the Nernst-Planck equation in molar units:

$$\frac{\partial c_i}{\partial t} = -u\nabla.c_i + D_i\ \nabla.\left(\vec{\nabla}c_i + \frac{z_i F}{RT}c_i\ \vec{\nabla}\ \psi\right) \tag{28}$$

The Nernst Planck equations gives the transport of each ion influenced by diffusion, electromigration and convection. Can be seen that the equations give two incognits, the ion concentration and the electrical potential the electric potential is described by the Poisson equation explained before

$$-\nabla.\left(\varepsilon\ \nabla\ \psi\right) = \sum_i \rho_i \tag{29}$$

Where ε is the electric permittivity of the double layer and the ρ_i is the charge density. The charge density in the case of NF membranes can be defined as a sum of the charge density of the ions and the fix charge density of the membrane:

$$\sum_i^N \rho_i = \sum_i^N z_i e c_i + \rho_{fix} \tag{30}$$

Supposing a cylindrical pore membrane, the fixed charge of the membrane expressed in terms of concentration is

$$\rho_{fix} = \frac{2\,\sigma}{F\,r_p} \tag{31}$$

Where σ is the surface charge density, F is the Faraday's constant and r_p is the pore radius.

Rewriting the Poisson equation gives:

$$-\nabla \cdot (\varepsilon_0 \varepsilon_r\, \nabla\, \psi) = \sum_i^N z_i e c_i + \rho_{fix} \tag{32}$$

Where $\varepsilon_r \varepsilon_r$ is the product by the permittivity of vacuum and the membrane or solvent.

The Poisson-Nernst-Planck equations that describes the ion transport results a nonlinear system of hyperbolic-elliptic partial differential equations. The system resulting is:

$$\frac{\partial c_i}{\partial t} = -u\nabla \cdot c_i + D_i\, \nabla \cdot \left(\vec{\nabla} c_i + \frac{z_i F}{RT} c_i\, \vec{\nabla}\, \psi \right) \tag{33}$$

$$-\nabla \cdot (\varepsilon_0 \varepsilon_r\, \nabla\, \psi) = \sum_i^N z_i e c_i + \rho_{fix} \tag{34}$$

The velocity u obeys the Navier-Stokes equations

$$\frac{\partial u}{\partial t} + u.\vec{\nabla}u - \vartheta \, \nabla^2 u + \vec{\nabla}P \; = \rho_i \, \vec{E} \tag{35}$$

Where ϑ is the kinematic viscosity, P the pressure and E is the electric field $\vec{E} = -\vec{\nabla}\,\psi$. The right-hand side of the equation is the Lorentz force that is the influence of the electrical field to the fluid.

The system of Poisson, Nernst-Planck and Navier Stokes equations was called by Osterle and co-workers space charge model (SC) [10]. This system of nonlinear partial differential equation in 2-D requires much computational resources. For that many simplifications are considered to solve these equations, the first is to reduce the system in 1-D, neglecting the radial variation, this assumption is valid when the Debye length is larger than the pore membrane. Another consideration is to suppose that the velocity is constant or that have a laminar profile ignoring the viscous effects and the force gradients that act to the fluid. With this assumption the Navier Stokes can be ignored.

The third assumption is the electroneutrality condition in all the regions of the system. This assumption considers that there's not charge separation anywhere in solution and so neutrality is maintained in all the system. When charges separation occurs, coulombic force influences the transport of ions described by the Poisson and Nernst-Planck equations.

For describe the electroneutrality condition analytically must be done by the dimensional analysis in Poisson equation [11]. The electrical potential can be normalized by the ratio with electrical potential and the thermal voltage, and the concentration by the bulk concentration $c_{i,\infty}$ of the electrolyte.

$$\Psi = \frac{e\,\psi}{K_b T} = \frac{F\,\psi}{R\,T} \tag{36}$$

$$\theta = \frac{c_i}{c_{i,\infty}} \tag{37}$$

$$-\nabla.\left(\varepsilon_0 \varepsilon_r \,\vec{\nabla}\,\psi\right) = \sum_i^N z_i F c_i \tag{38}$$

With the non-dimensional concentration and electrical potential, the Poisson equation can be written as

$$-\nabla \cdot (\vec{\nabla}\,\psi) = \frac{F^2 c_{i,\infty}}{\varepsilon\,R\,T} \sum_{i}^{N} z_i c_i \tag{38.1}$$

The Poisson equation in that form gives also the same parameter that in the Debye-Hückel theory explained before, the Debye length

$$\kappa = \left(\frac{F^2\,c_{i,\infty}}{\varepsilon\,R\,T} \right)^{1/2} \tag{39}$$

$$\kappa^{-1} = \lambda_D = \left(\frac{\varepsilon\,R\,T}{F^2 c_{i,\infty}} \right)^{1/2} \tag{39.1}$$

The Poisson equation rewritten in terms of the Debye length

$$-\lambda_D{}^2\,\nabla^2\psi = \sum_{i}^{N} z_i c_i \tag{40}$$

The Debye length as be stated before indicates the length of the electrical double layer. If there are charge separation, the electrical field can vary, and hence over which $\nabla^2\psi$ can take a large value, is limited by the Debye length [12].

Considering that the Debye length is very small compared to the other length scales of the system, the Poisson equation gives

$$\lambda_D^2\,\frac{\partial^2\,\Psi}{\partial x^2} \cong 0 \tag{41}$$

And gives the electroneutrality condition

$$\sum_i z_i c_i = 0 \tag{42}$$

If the system has fixed charge density like a membrane, the electroneutrality condition gives

$$\sum_i z_i e c_i + \rho_{fix} = 0 \tag{43}$$

The physical significance of this equality is that there is no local accumulation of charge in all the points of the system. The gradient of electrical potential is important to consider interactions with small particles and charges surface phenomena but is generally unimportant with the bulk solution. The electroneutrality condition implies that the potential distribution is governed by Laplace's equation($\nabla^2 \psi = 0$), because the right-hand side of the Poisson equation is 0 [12].

Can be observed that the electroneutrality condition gives a paradox, because that one cannot use both Poisson's equation and the electroneutrality condition, this over specifies the problem.

In summary, the electroneutrality condition will never be applicable very close to a boundary where charge separation takes place like in the electrical double layer where the gradient of the electrical field become very large.

1.3.1. NERNST PLANCK WITH STERIC EFFECTS

Also an important phenomena that appears in the selective membranes is the steric effect, making this crucial for what type of molecules can pass through the membrane. The steric effect is based in the length of the pores and the ions, basically arise from a fact that each ion occupies a certain amount of space, for this reason the ions interact with them and with the

membrane, because the smaller ions will be able to pass through the membrane, but the ions with bigger radius than the pore radius can't be able to pass.

But the Nernst-Planck equations are based to dilute solution theory, that assumes the ions don't interact with them and her movement is independent between the other ions. For this reason the statistical-physics scientists developed a modification to Nernst-Planck equations based on variation of free energy:

Kinetic energy   Entropy   Electric energy   steric energy

$$E = \int (\frac{\rho}{2} u^2 + K_b T \sum_i^N c_i \log c_i + \frac{1}{2} (\sum_i^N z_i e c_i + e\, \rho_{fix}) \psi) dx + \sum_{i,j=1}^N g_{ij} \int c_i c_j dx \tag{44}$$

Classical PNP

PNP with steric effects

The Nernst Planck equations with steric effects can be written as

$$\frac{\partial c_i}{\partial t} = -u\nabla . c_i + D_i \, \nabla . \left(\vec{\nabla} c_i + \frac{z_i F}{RT} c_i \, \vec{\nabla} \psi + \frac{c_i}{RT} \sum_j^N g_{ij} \nabla \, c_j \right) \tag{45}$$

Where the coefficient g_{ij} is

$$g_{ij} = \epsilon_{ij} (a_i + a_j)^{12} \tag{46}$$

Where ϵ_{ij} is a coefficient that depends of molecular interactions that only be adjusted to reproduce experimental data or calculated from quantum mechanics, and a are the diameter of the ions.

The equation approximates the repulsive term of the Lenard Jones (LJ) potential added to the concentration flux. The LJ is a well-known mathematical model for describing the interaction between a pair of ions, and in this work is used to describe the steric effects of the ions [13].

1.3.2.   TEORELL-MEYER-SIEVERS

TMS model is a less rigorous model compared to the SC model explained before, but it has large applicability in the case of NF membranes.

The model assumes:

- Radial variation negligible (1-D)
- Convective flow constant
- Local Electroneutrality condition
- Uniform distribution of fixed charges
- Membrane and adjacent solution interfaces are in Donnan equilibrium
- Steady state

In TMS model can be seen that the three simplifications explained in the las section are applied. Also supposes that the fixed charge density is distributed uniformly, and the most important statement of this model is that supposes a Donnan equilibrium is given in the interfaces of the solution and the membrane.

The Donnan equilibrium is based when ions are too large to pass through the membrane, these ions are accumulated in the interface attracting ions of opposite charge and repelling ions of the same charge, for this reason appears an electrical and concentration gradient, these gradients are equal but with opposite sign. In the equilibrium, the product of the ionic concentrations of each side of the membrane are constant.

In the absence of the Poisson equation for describe the transport of ions through the membrane, the Donnan theory can be able to describe the concentration profiles in the interface with partition coefficients obtained from the Donnan equilibrium. This concept is explained in the following figure.
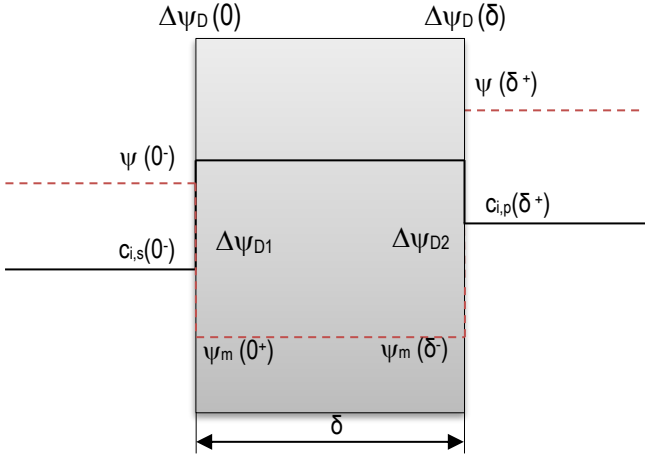
Figure 12. Schematic figure of the TMS model

In the figure can be seen that the concentration suffers a jump in the interface caused by the difference of the electrical potential between the solution and the membrane, the electrical potential in the interface is called Donnan potential.

The Donnan equilibrium must be explained by the dilute solution theory. At equilibrium the electrochemical potential in the two phases must be equal.

$$\tilde{\mu}_i = \mu_{0,s} + RT \ ln\frac{c_{i,s}}{c_{i,0}} + z_i F \ \psi_s = \mu_{0,m} + RT \ ln\frac{c_{i,m}}{c_{i,0}} + z_i F \ \psi_m \qquad (47)$$

This model states that the surface potential is at Donnan equilibrium, this assumption makes the $\Delta\psi_D$ constant . The equality can be written in the form of a constant partition constant.

$$\frac{c_{i,m}}{c_{i,s}} = e^{-z_i F \ \Delta\psi_D/_{RT}} = \beta_i = \text{constant} \qquad (48)$$

Note that the equation gives a distribution of Boltzmann with the Donnan potential. With this partition coefficient the concentration ion in the boundary membrane can be calculated with the concentration in the solution interface.

The equations that describes the profile concentration and the electrical potential in the TMS models are the Nernst-Planck equation and the electroneutrality condition based it on the Poisson equation.

The flux defined by the Nernst-Planck equation is

$$F_i = -D_i \left(\frac{dc_i}{dx} + \frac{z_i F}{RT} c_i \frac{d\psi}{dx} \right) + u c_i \tag{49}$$

The flux is described by diffusion, electromigration and the convective flow, in the steady state the flux is constant, note that in this case the derivative is total and not a partial derivative like the transient case. And the electroneutrality condition in the solvent and the permeate solution:

$$\sum_i^N z_i C_{i,s} = 0 \qquad \sum_i^N z_i C_{i,p} = 0 \tag{50.a}$$
$$\tag{50.b}$$

The electroneutrality condition in the membrane

$$\sum_i^N z_i c_{i,m} + \rho_{fix} = 0 \tag{51}$$

The molar and volume fluxes are described by the filtration condition which relates the concentration of the permeate and the ionic and volume fluxes in the steady State

$$F_i = u\, C_{i,p}(\delta^+) \tag{52}$$

Inserting to the equation of the flux gives

$$u\, C_{i,p}(\delta^+) = -D_i \left(\frac{dc_i}{dx} + \frac{z_i F}{RT} c_i \frac{d\psi}{dx} \right) + u c_i \tag{53}$$

Can be written as

$$\frac{dc_i}{dx} = \frac{u}{D_i}\left(c_i - C_{i,p}(\delta^+)\right) - \frac{z_i F}{RT} c_i \frac{d\psi}{dx} \tag{54}$$

Multiplying the equation by z_i and derive the electroneutrality equation in the membrane the equation can be written as sum of all the ions

$$\sum_{i=1}^{N} z_i \frac{dc_i}{dx} = \sum_{i=1}^{N} \left(z_i \frac{u}{D_i}\left(c_i - C_{i,p}(\delta^+)\right) - \frac{F}{RT} z_i^2 c_i \frac{d\psi}{dx}\right) = 0 \tag{55}$$

The electrical potential can be written as

$$\frac{d\psi}{dx} = \frac{\sum_{i=1}^{N} z_i \frac{u}{D_i}\left(c_i - C_{i,p}(\delta^+)\right)}{\frac{F}{RT}\sum_{i=1}^{N} z_i^2 c_i} \tag{56}$$

Considering the case of 1:1 electrolyte the equation obtained is

$$\frac{d\psi}{dx} = \frac{z_1 \frac{u}{D_1}\left(c_1 - C_{1,p}(\delta^+)\right) - z_2 \frac{u}{D_2}\left(c_2 - C_{2,p}(\delta^+)\right)}{\frac{F}{RT}\left(z_1^2 c_1 + z_2^2 c_2\right)} \tag{57}$$

The electroneutrality conditions in this gives the following relations

In the solute

$$z_1 C_{1,s}(0^+) + z_2 C_{2,s}(0^+) = 0 \longrightarrow C_{2,s}(0^+) = -\frac{z_1 C_{1,s}(0^+)}{z_2} \tag{58}$$

In the permeate

$$z_1 C_{1,p}(\delta^+) + z_2 C_{2,p}(\delta^+) = 0 \longrightarrow C_{2,p}(\delta^+) = -\frac{z_1 C_{1,p}(\delta^+)}{z_2} \tag{59}$$

In the membrane

$$z_1 c_1(x) + z_2 c_2(x) + \rho_{fix} = 0 \longrightarrow c_2(x) = -\frac{z_1 c_1(x) + \rho_{fix}}{z_2} \tag{60}$$

With these relations the equation can be written in terms of only one ion

$$\frac{d\psi}{dx} = \frac{z_1 u \left(\frac{1}{D_1} - \frac{1}{D_2}\right) c_1(x) - z_2 u \left(\frac{1}{D_1} - \frac{1}{D_2}\right) C_{1,p}(\delta^+) - \frac{u \, \rho_{fix}}{D_2}}{\frac{F}{RT} \left(z_1^{\,2} c_1(x) - z_2 z_1 c_1(x) + z_2 \rho_{fix}\right)} \tag{61}$$

With the electrical potential defined the equation of concentration profile can be solved

$$\frac{dc_1(x)}{dx} = \frac{u}{D_i} \left(c_1(x) - C_{1,p}(\delta^+)\right) - \frac{z_1 F}{RT} c_1(x) \frac{d\psi}{dx} \tag{62}$$

For solve the electrical potential and concentration equation must be defined one boundary condition for each one, because they only have one derivative, the boundary condition must be the concentration of the solvent, and then with the Donnan partition coefficient describes the jump across the interface membrane.

This reason makes this model easier than the PNP equations, but the model only allows to describe the concentration and potential profiles inside the membrane because assumes that the concentration in the solvent and in the permeate are constant.

These equations are simpler than the PNP equations, but have non-lineal terms making difficult to solve analytically the equations. Usually are solved numerically by the Runge-Kutta method, in some works supposed that the profile in the membrane is lineal making the spatial

derivative the thickness of the membrane and turn the equations simpler to solve in analytic way.

For understand clearly the difference between the PNP equations and the TMS model, the following figure shows a qualitative profile of ions concentration with the two theories.
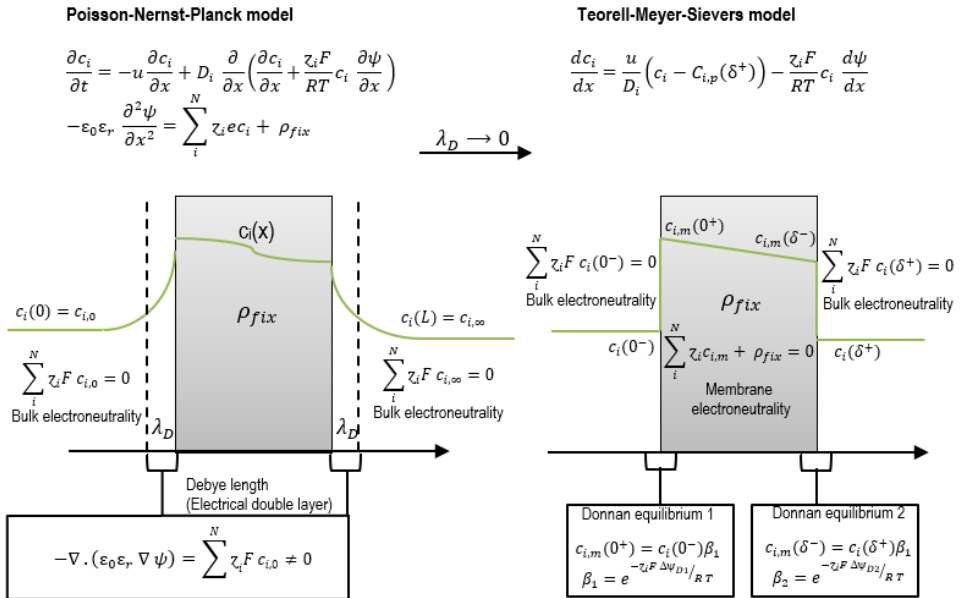

Figure 13. Differences between the PNP model and the TMS model

The idea of the Donnan potential can be explained with capacitors theory, imagine two parallel plate with opposite charge separated by a distance λ_D that represents the Deby length. This system represents the interface between positive ions and a membrane with negative surface charge.

$$-\lambda_D{}^2 \, \nabla^2 \psi = \sum_i^N z_i c_i \qquad \xrightarrow{\lambda_D \to 0} \qquad -\nabla^2 \psi = \infty$$
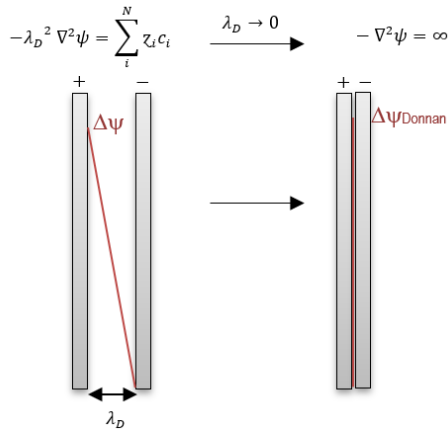
Figure 14. Description of the electrical double layer like a parallel plate with opposite charge

The simplicity to solve TMS model makes very attractive to be implemented in modelling of NF membranes, but due the simplifications that assumes makes difficult to predict the behavior of the ions. For this reason, many modifications are implemented to the TMS model for make it more realistic.

The extended Nernst-Planck equation was proposed by Schlogyl, Dresner, and Johnson [14], is the classical NP equation but adding hindrance coefficients in the diffusion coefficient and in the convective flow and take account to steric and dielectric effects.

These hindrance factors are considered to take count the steric effect at the pores membrane, if a ion with a bigger diameter than the pore radius can't pass through it, also the ion diffuses very different in a solution than in a pore membrane, in the pore membrane the ion bounces in the walls of the pore making the diffusion coefficient different.
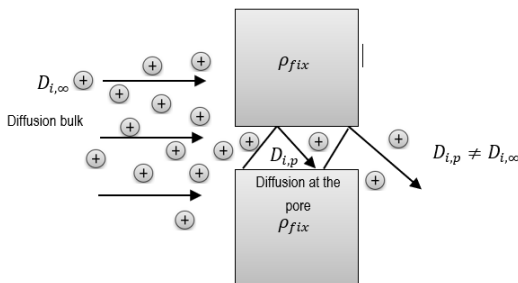

Figure 15. Description of the difference of the diffusivity between the bulk and the pores.

For describe the variations of diffusion coefficient and in the convective flux. These are corrected with the hindrance factors, both dependent on the ratio of solute radius and to pore radius. For de convective flux the hindrance factor to take account the effects of the pore on the species motion by the following equation [15]:

$$K_{i,c} = (2 - \varphi_{steric})\left(1 + 0.054\,\lambda_i + 0,988\,\lambda_i{}^2 + 0,441\,\lambda_i{}^3 \right) \tag{63}$$

Where φ_{steric} is the dimensionless steric partition coefficient of the ion expressed as

$$\varphi_{steric} = (1 - \lambda_i)^2 \tag{64.a}$$

And λ_i is the ratio of the ionic radius by the pore radius

$$\lambda_i = \frac{r_i}{r_p} \tag{64.b}$$

For the diffusive effects, the hindrance factor is defined as

$$K_{i,D} = \left(1 - 2,30\,\lambda_i + 1,154\,\lambda_i{}^2 + 0,224\,\lambda_i{}^3 \right) \tag{65}$$

The diffusion and the convective flow in the membrane are corrected with the hindrance factors by the following form

$$D_{i,p} = K_{i,D}D_{i,\infty}\frac{\eta_o}{\eta} \tag{66.a}$$

$$u_p = K_{i,c}\,u \tag{66.b}$$

Where $D_{i,\infty}$ is the diffusion coefficient in the bulk, u the velocity, η_o the viscosity in the bulk and η is the viscosity affected by the effect of the pore membrane, the ratio $\frac{\eta_o}{\eta}$:

$$\frac{\eta_o}{\eta} = 1 + 18\left(\frac{d}{r_p}\right) - 9\left(\frac{d}{r_p}\right)^2 \tag{66.c}$$

When the pore radius decreases, the viscosity of the solution increases. The steric effect and the dielectric effect are very important to take account in the interface of the solution and the membrane because the steric and dielectric effects have a crucial decision that what ions can pass through the membrane and not.

For this reason, the partition coefficient in the interface based on the Donnan equilibrium is modified adding the steric and dielectric effects as

$$\frac{c_{i,m}}{c_{i,s}} = e^{-z_i F \, \Delta\psi_D/R\,T} \, \varphi_{steric} \, \beta_{dielectric} \tag{67}$$

The steric partition coefficient was defined, the dielectric partition coefficient is described by the Born model.

$$\beta_{dielectric} = e^{-\Delta W_i/K_b\,T} \tag{68.a}$$

Where ΔW_i is the energy solvation barrier of the ion in the interface and is defined by the Born model as

$$\Delta W_i = \frac{(z_i F)^2}{8\,\pi\,\varepsilon_o\,r_i}\left(\frac{1}{\varepsilon_p} - \frac{1}{\varepsilon_b}\right) \tag{69}$$

Where ε_b is the electric permittivity of the bulk and ε_p is the electric permittivity of the pores.

This equation based on the Poisson-Boltzmann equation describes the solvation energy barrier that is formed by the effects to the interaction of ions with the polarized surface membrane due to the difference of their dielectric constant [16].

With these modifications the model is known as DSPM-DE (Donnan Steric Pore Model – Dielectric effect). With the corrections the equations can be written as

$$\frac{dc_i}{dx} = \frac{K_{i,c}\,u}{D_{i,p}}\left(c_i - C_{i,p}(\delta^+)\right) - \frac{z_i F}{RT}\,c_i\,\frac{d\psi}{dx} \tag{70}$$

This model has been identified very appropriate and accurate for the characterization of the NF membranes because with the empirical coefficient is able to correct the error produced by the simplifications considered in TMS theory.

2. OBJECTIVES

The main objective of the work is to propose a model of ion transport in a generalized way and solve it with the minimum of simplifications.

The transport phenomena model proposed for describe the behaviour of ions, in our case NaCl, through a nanofiltration membrane is the system of partial differential equations of Poisson and Nernst-Planck including steric effects and in 1-D in transient.

The system of partial differential equations will be solved by means of numerical algorithms with the Wolfram Mathematica program. The results will be compared with a more complex model (Poisson, Nernst-Planck and Navier Stokes in 2D) and a simpler model (Donnan-Steric-Partition-Dielectric exclusion model) to verify our work.

With the model validated many simulations will be done for view the effects of all the variables that depend the system.

3. MEMBRANE MODEL

The system to model in this work is the transport of two symmetric ions ($|z_+| = |z_-|$) in this case Na+ and Cl- in a NF membrane described by the Poisson-Nernst-Planck system in 1-D. In this work is assumed that the velocity is constant making simpler the computational complexity because the Navier-Stokes equation is not considered. The system of equations for two symmetrical ions with opposite charge are:

$$\frac{\partial c_{Na^+}}{\partial t} = -u\frac{\partial c_{Na^+}}{\partial x} + D_{Na^+}\frac{\partial}{\partial x}\left(\frac{\partial c_{Na^+}}{\partial x} + \frac{z_i F}{RT}c_{Na^+}\frac{\partial \psi}{\partial x}\right) \tag{71}$$

$$\frac{\partial c_{Cl^-}}{\partial t} = -u\frac{\partial c_{Cl^-}}{\partial x} + D_{Cl^-}\frac{\partial}{\partial x}\left(\frac{\partial c_{Cl^-}}{\partial x} + \frac{z_i F}{RT}c_{Cl^-}\frac{\partial \psi}{\partial x}\right) \tag{72}$$

Considering the Nernst-Planck equations with steric effects

$$\frac{\partial c_{Na^+}}{\partial t} = -u\frac{\partial c_{Na^+}}{\partial x} + D_{Na^+}\frac{\partial}{\partial x}\left(\frac{\partial c_{Na^+}}{\partial x} + \frac{z_i F}{RT}c_{Na^+}\frac{\partial \psi}{\partial x} + \frac{c_{Na^+}}{RT}\sum_j^N g_{ij}\frac{\partial c_j}{\partial x}\right) \tag{73}$$

$$\frac{\partial c_{Cl^-}}{\partial t} = -u\frac{\partial c_{Cl^-}}{\partial x} + D_{Cl^-}\frac{\partial}{\partial x}\left(\frac{\partial c_{Cl^-}}{\partial x} + \frac{z_i F}{RT}c_{Cl^-}\frac{\partial \psi}{\partial x} + \frac{c_{Cl^-}}{RT}\sum_j^N g_{ij}\frac{\partial c_j}{\partial x}\right) \tag{74}$$

Where

$$\sum_j^N g_{ij}\frac{\partial c_j}{\partial x} = g_{Na^+}\frac{\partial c_{Na^+}}{\partial x} + g_{Cl^-}\frac{\partial c_{Cl^-}}{\partial x} \tag{75}$$

The Poisson equation

$$-\varepsilon_0\varepsilon_r\frac{\partial^2\psi}{\partial x^2} = z_{Na^+}Fc_{Na^+} + z_{Cl^-}Fc_{Cl^-} + \rho_{fix} \tag{76}$$

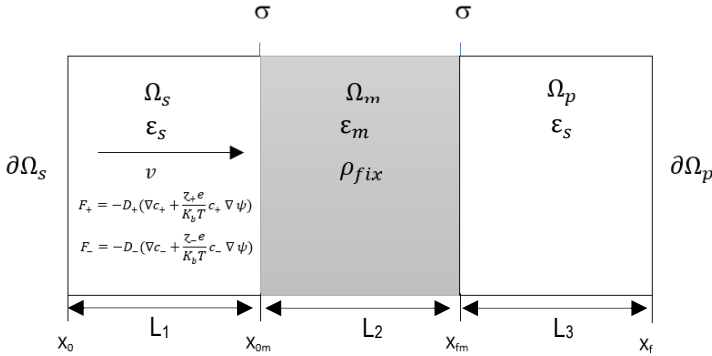The one-dimensional system can be described with this scheme:

Figure 16. Model membrane system.

A planar membrane with a fix charge density and surface charge separates two aqueous solutions of Na+ and Cl-. The dielectric permittivity is different between the solution and the membrane.

The boundary conditions of the reservoirs are located at $\partial\Omega_s$ and $\partial\Omega_p$ respectively, and the flux is normal to the axial direction of membrane.

And the fixed charge density of the membrane is defined as:

$$\rho_{fix} = \begin{cases} 0 & \Omega_s \\ \rho_{fix} & \Omega_m \\ 0 & \Omega_p \end{cases} \qquad (77)$$

The system of equations is solved in dimensionless form because by transforming a PDE in dimensionless form all the parameters that governing the system are reduced to only a few dimensionless numbers. For example, making the Navier-Stokes dimensionless, can be seen that the governing parameters are reduced to the Reynolds number, what is quite advantageous.

The system of PNP equations are non-dimensionless by the Pi Buckingham theorem that can be viewed with more detail in the Appendix 2.

The dimensionless PNP equations gives

$$\frac{\partial \theta_{Na^+}}{\partial t} = -Pe_{Na^+} \frac{\partial \theta_{Na^+}}{\partial x} + \frac{\partial}{\partial x}\left(\frac{\partial \theta_{Na^+}}{\partial x} + \theta_{Na^+} \frac{\partial \Psi}{\partial x} \right) \tag{78}$$

$$\frac{\partial \theta_{Cl^-}}{\partial t} = -Pe_{Na^+} \frac{\partial \theta_{Cl^-}}{\partial x} + \frac{\partial}{\partial x}\left(\frac{\partial \theta_{Cl^-}}{\partial x} - \theta_{Cl^-} \frac{\partial \Psi}{\partial x} \right) \tag{79}$$

$$\frac{\partial \theta_{Na^+}}{\partial t} = -Pe_{Na^+} \frac{\partial \theta_{Na^+}}{\partial x} + \frac{\partial}{\partial x}\left(\frac{\partial \theta_{Na^+}}{\partial x} + \theta_{Na^+} \frac{\partial \Psi}{\partial x} + \frac{\theta_{Na^+}}{RT} \sum_j^N g_{ij} \frac{\partial \theta_j}{\partial x} \right) \tag{80}$$

$$\frac{\partial \theta_{Cl^-}}{\partial t} = -Pe_{Na^+} \frac{\partial \theta_{Cl^-}}{\partial x} + \frac{\partial}{\partial x}\left(\frac{\partial \theta_{Cl^-}}{\partial x} - \theta_{Cl^-} \frac{\partial \Psi}{\partial x} + \frac{\theta_{Cl^-}}{RT} \sum_j^N g_{ij} \frac{\partial \theta_j}{\partial x} \right) \tag{81}$$

$$\tilde{\lambda}_D^2 \frac{\partial^2 \Psi}{\partial \xi^2} = \theta_{Na^+} - \theta_{Cl^-} + \zeta_{fix} \tag{82}$$

Where

$\Psi = \dfrac{F\,\psi}{R\,T}$		Dimensionless electrical potential
$\tau = \dfrac{L^2}{D\,t}$		Dimensionless time scale
$\xi = \dfrac{x}{L}$		Dimensionless length scale
$Pe = \dfrac{u\,L}{D}$		Peclet Number
$\tilde{\lambda}_D^2 = \left(\dfrac{\lambda_D}{L}\right)^2 = \dfrac{\varepsilon\,R\,T}{L^2 \sum_i^N F^2 c_{i,\infty}} = \dfrac{\varepsilon\,R\,T}{L^2\,2\,F^2\,I}$		Dimensionless Debye length (electrical double layer)
$\theta = \dfrac{c}{Co}$		Dimensionless concentration
$\zeta_{fix} = \dfrac{\rho_{fix}}{F\,Co}$		Dimensionless fixed charge

In dimensionless form can be seen that all the parameters of the system only depends of the Peclet Number (is the ratio of the convective term by the diffusive term, and describes the Taylor-Aris dispersion of the system) and the dimensionless Debye length that describes the electric interactions of the ions in the electrical double layer.

Note that these parameters depend by physical constants and by parameters that depends of the system specified, with dimensionless form if the system is different only affect the dimensionless parameters.

The most difficult thing to solve of this system of equations is to specify correctly the boundary conditions at the limit of reservoirs and the interface conditions. In this work the boundary conditions and the initial conditions for solve the PDE's are

Type	BC's	Physical significance	Boundary
Dirichlet	$c_{Na^+}(0) = c_{Na^+,\infty}$ $\theta_{Na^+}(0) = 1$	Initial concentration at the boundary	$\partial\Omega_s$
Dirichlet	$c_{Cl^-}(0) = c_{Cl^-,\infty}$ $\theta_{Cl^-}(0) = 1$	Initial concentration at the boundary	$\partial\Omega_s$
Dirichlet	$\psi(0) = 0$ $\Psi(0) = 0$	No current at the boundary	$\partial\Omega_s$
Neumann	$\left(-uc_{Na^+}+D_{Na^+}(\frac{\partial c_{Na^+}}{\partial x}+\frac{z_i F}{RT}c_{Na^+}\frac{\partial \psi}{\partial x})\right)\Big|_{x=L} = 0$ $\left(-Pe_{Na^+}\frac{\partial \theta_{Na^+}}{\partial x}+\frac{\partial \theta_{Na^+}}{\partial x}+\theta_{Na^+}\frac{\partial \Psi}{\partial x}\right)\Big|_{x=L} = 0$	No flux at the boundary	$\partial\Omega_p$
Neumann	$\left(-uc_{Cl^-}+D_{Cl^-}(\frac{\partial c_{Cl^-}}{\partial x}+\frac{z_i F}{RT}c_{Cl^-}\frac{\partial \psi}{\partial x})\right)\Big|_{x=L} = 0$ $\left(-Pe_{Cl^-}\frac{\partial \theta_{Cl^-}}{\partial x}+\frac{\partial \theta_{Cl^-}}{\partial x}+\theta_{Cl^-}\frac{\partial \Psi}{\partial x}\right)\Big|_{x=L} = 0$	No flux at the boundary	$\partial\Omega_p$
Neumann	$\frac{\partial \psi}{\partial x}\Big|_{x=L} = 0$ $\frac{\partial \Psi}{\partial x}\Big|_{x=L} = 0$	No current flux at the boundary	$\partial\Omega_p$

Note that for the Neumann boundary conditions of the ions appears the current flux, but with the no current flux condition at the boundary, makes 0 this term. But is written in the general form the flux.

It's obviously that the analytic solution of this system of equations is not possible and must be solved with numerical methods.

Numerical solution of partial differential equations (PDE) can be schematized in the following diagram:
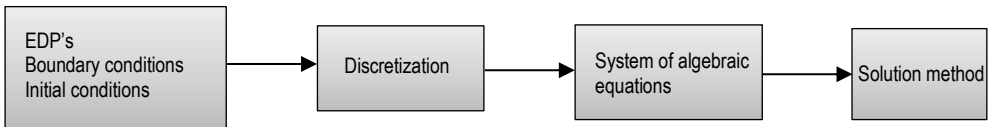

Figure 17. Scheme of numerical solutions of PDE's

The first thing to do is convert the PDE's into a system of algebraic equations, and the boundary condition in discrete algebraic equations, this process is called discretization. There are many methods of discretization, the most common used are the finite difference method, the finite element method and spectral methods.

In this work we implement the finite difference method for discretize the equations and for solve the System of PDE is used the Method of Lines in the Mathematica code.

The numerical Method of Lines is a technique for solving partial differential equations by discretizing one dimension and then integrate the semi-discretized problem as a system of Ordinary Differential Equations (ODE's) or Differential Algebraic Equations (DAE's).

The only restriction for use this method is that the PDE problem must be an initial value problem (Cauchy), because the ODE and DAE integrators used are initial value problem solvers. This rules out purely elliptics equations like Poisson equations but in this work the Poisson equation is coupled with the Nernst-Planck equations and that fact makes the Poisson equations dependent of time and can be considered a Cauchy problem.

For implement finite difference schemes to discretize in Mathematica we used an algorithm proposed by [17], where is extensively explained in the Appendix 1: Mathematical method.

Where is compared the algorithm with the analytical solution of the diffusion equation, first with Dirichlet boundary conditions and the second with Neumann boundary conditions for make sure that the method is consistent with different conditions.

4. RESULTS AND DISCUSSION

4.1. MODEL VALIDATION

First, the numerical solution must be compared with analytic or numerical solution that are validated with experimental data.

The numerical solution is compared with the numerical solution of Allen. T, Hong.L. *A charged nanoporous model for nanofiltration*. Dept. of Applied Math. Feng Chia University. Allen and Hong modeled the NF membrane by the most complex model, the SC (space charge model) in 2D.

Allen and Hong computational domain 2D
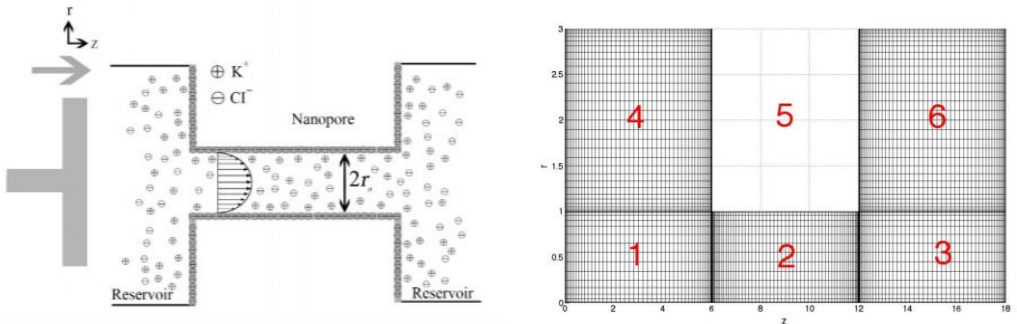
Figure 18. Membrane domain of Allen and Hong project.
via: https://www.tims.ntu.edu.tw/download/talk/120604_Tzyy-Leng%20Horng.pdf

Can be seen that the 2D system of 18 nm of length is represented by two reservoirs (6nm each one) and a charged membrane with 6 nm of length with a pore of 2r of diameter, the boundary conditions at the walls is zero flux, in the reservoirs are applied the same boundary conditions as this project.

A comparison table between the model of this project and the project of Allen and Hong

	This project	Allen and Hong project
Dimensions	1D	2D
Equations	1. Poisson equation 2. Nernst-Planck or Modified Nernst-Planck with steric effects	1. Poisson equation 2. Nernst-Planck or Modified Nernst-Planck with steric effects 3. Navier-Stokes

Parameters used for comparing the numerical method (view page 37 of Allen and Hong).

(Note: In Allen and Hong project the ions that are modelled are K+ and Cl-, the only difference between sodium and potassium to take account are the diffusivity and the ion radius:

[KCl] = 0.011982M $c_{K^+,\infty} = 0.011982M$ $c_{Cl^-,\infty} = 0.011982M$	Initial concentration
r_p= 2nm	Pore radius
D_{Na^+}= 1.33 10^{-9} m^2/s D_{Cl^-}= 2 10^{-9} m^2/s $D_{i,pore}$=0.25 $D_{i,bulk}$	Diffusivity in the pore and the bulk
u_o / u_{ref} =0.03 where u_{ref} = 0.97850 m/s	Dimensionless velocity
$\tilde{\sigma}$ =-2	Dimensionless surface charge $$\tilde{\sigma} = \frac{\sigma}{C_o F \, r_p}$$
T= 293.15 K	Temperature
$\varepsilon_0 \varepsilon_{bulk} = 78.5 \, \varepsilon_0$ water $\varepsilon_0 \varepsilon_{pore} = 80 \, \varepsilon_0$	Permittivity of the solvent and the bulk. Where ε_0 = 8.85 10^{-12} F/m Is the permittivity of vacuum
L= 18 nm	Length of the system

The diffusion coefficients, and the velocity, dielectric permittivity and the fixed charge density are modelled as Heaviside functions, for differentiate the parameters that are different depending on the region:

$$u = \begin{cases} u & \Omega_s \\ u_{pore} & \Omega_m \\ u & \Omega_p \end{cases} \qquad D_i = \begin{cases} D_{bulk} & \Omega_s \\ D_{pore} & \Omega_m \\ D_{bulk} & \Omega_p \end{cases}$$

$$\varepsilon_0 \varepsilon_{bulk} = \begin{cases} \varepsilon_0 \varepsilon_{bulk} & \Omega_s \\ \varepsilon_0 \varepsilon_{pore} & \Omega_m \\ \varepsilon_0 \varepsilon_{bulk} & \Omega_p \end{cases} \qquad \rho_{fix} = \begin{cases} 0 & \Omega_s \\ \rho_{fix} & \Omega_m \\ 0 & \Omega_p \end{cases}$$

The velocity in the membrane is calculated with the equations (58) in the section 1.3.2. Note that the model is in dimensionless form, so the dimensionless parameters like the Peclet number also varying in the axial direction.

For example, the diffusion coefficient of the ion sodium has this form in the axial direction
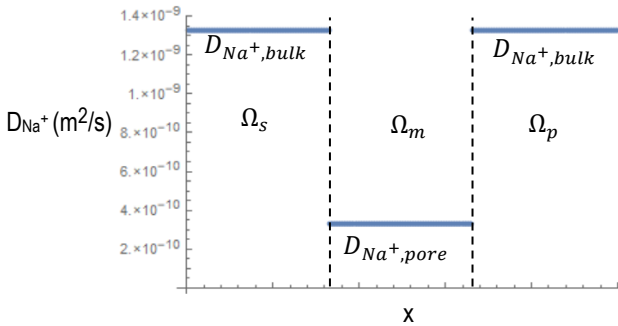

Figure 19. Diffusivity of sodium in the pore in this case $D_{pore} = 0.25\ D_{bulk}$.

With all the parameters used in one of the examples of Allen and Hong project, the solution can be compared with our numerical solution.
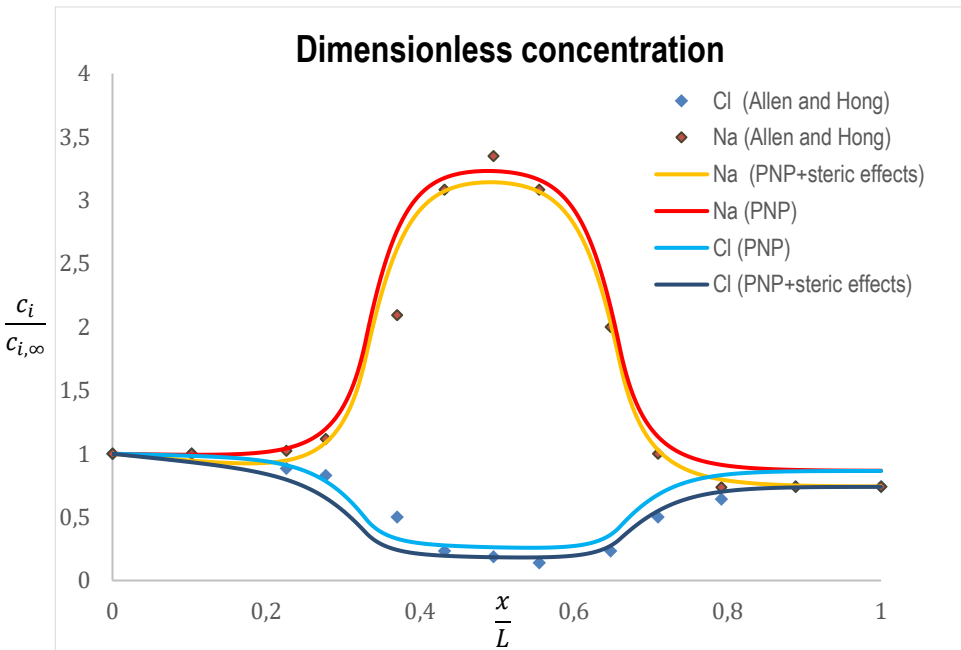
Figure 20. Comparison between the numerical solution of Allen and Hong project (points) and the numerical solution of this project.

At first glance, can be seen that the result of our model fits the Allen and Hong solution. But see that the solution of Poisson Nernst Planck equations it deviates slightly from the final concentration, because without the steric effects the Nernst-Planck equations in only one dimension they are not accurate enough to describe the system. Also, can be viewed that in the 2D model of Allen and Hong the ions are more sensible to the charge of the membrane making maxims and minims greater than our model.

But if we add the steric effects to the equations, it fits perfectly and correctly predicts the final concentration. In this case the steric coefficient selected is 0.02.

For compare the numerical solution with the DSPM-DE (Donnan Steric Partitioning model-Dielectric exclusion) model explained in the 1.3.2 section is selected a simulation with the DSPM-DE model that appears in the Allen and Hong project (page 76) where is solved with the

same parameters as before with a dimensionless fixed charge density = -4 and pore permittivity $\varepsilon_0 80$.
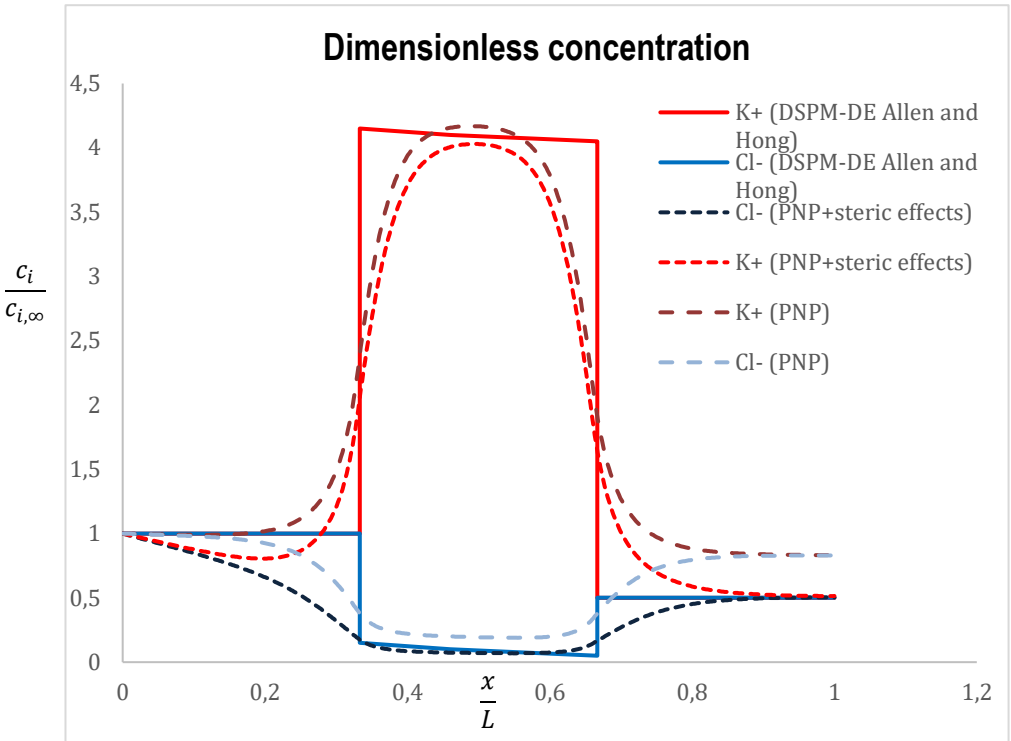
Figure 21. Comparison between the numerical solution of Allen and Hong solution of DSPM-DE model (lines) and the numerical solution of this project.

Can be seen that the numerical solution of PNP solution without steric effects can predict very good the tendency of the concentration of ions but cannot predict correctly the final concentration. The DSPM-DE model is not a good model for describe the interior of membrane because assume many simplifications explained in the section 1.3.2 but has a good acceptance to model the concentration of permeate of NF with all the relations at the interface.

But the PNP with steric effects can predict with exactitude the tendency and the final concentration, in this case the steric coefficient is 0.02. So if the DSPM-DE model is good for predict the concentration at the permeate and the PNP the comportment of the ions in the

membrane, a good way to modelized NF membranes can be in the first case model with the DSPM-DE model to find the final concentration of the ions, then solve the PNP equations and choose a steric coefficient that correct the PNP equations to find the final concentration.

As it be explained in the 1.3.2 section, the DSPM-DE model assumes electroneutrality in all the regions of the system, this can be seen making a plot of the density charge of the DSPM-DE model of Allen and Hong between the numerical solution of this project.
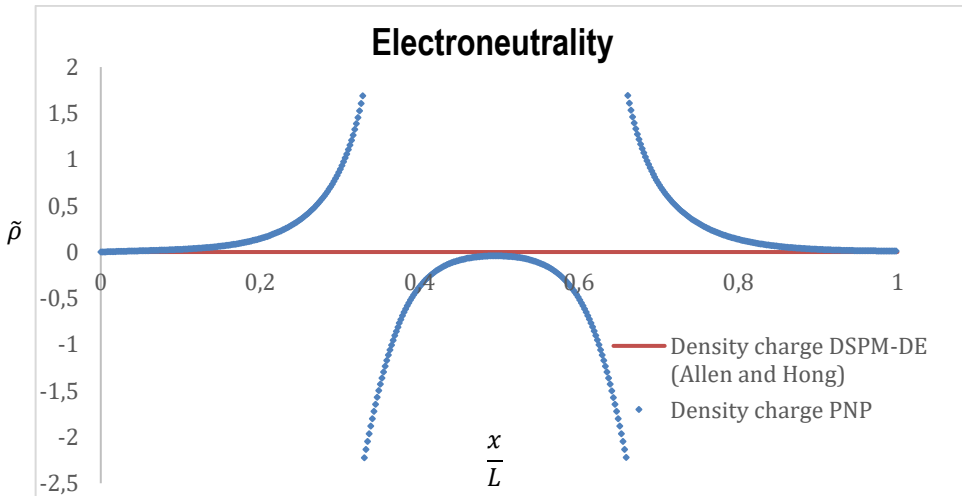
Figure 22. Comparison of the dimensionless charge density between the DSPM-DE model and the PNP model.

.

Can be seen that in the DSPM-DE model the electroneutrality the condition is fulfilled throughout the system, but in the PNP model the electroneutrality condition is only true in the bulk regions and in the centre of the membrane, this   this gives consistency to the Gouy Chapman's model that says that in the electrical double layer the gradients became very high and not satisfying the electroneutrality condition .

In the exterior interfaces of the membrane the density charge becomes positively high because the counter ions are attracted to the surface of the membrane.

In the interior interface of the membrane the density charge is very negative because the fixed charge of the membrane is higher than the concentration of the ions, in the centre of the membrane the concentration of ions is balanced making electroneutral the region.

4.2. **EFFECT OF VARIABLES**

Parameters used

[NaCl] = $(5 \times 10^{-3} - 3)$M	Initial concentration
r_p= 2nm	Pore radius
D_{Na^+}= 1.33 x 10^{-9} m^2/s D_{Cl^-}= 2 x 10^{-9} m^2/s $D_{i,pore} = K_{i,D}D_{i,\infty}\dfrac{\eta_o}{n}$	Diffusivity in the pore and the bulk
η_o= 1000 Kg / m^2	Viscosity
u= 0.03 m/s $u_{pore} = K_{i,c}u$	Dimensionless velocity
ζ_{fix}=(-0.1 to -2)	Dimensionless fixed charge of the membrane
T=293.15 K	Temperature
$\varepsilon_0\varepsilon_{bulk} = 78.5\,\varepsilon_0$ water $\varepsilon_0\varepsilon_{pore} = 80\,\varepsilon_0$	Permittivity of the solvent and the bulk. Where ε_0 = 8.85 10^{-12} F/m Is the permittivity of vacuum
L= 200 nm L$_1$= 50 nm L$_2$= 100 nm L$_3$= 50 nm	Length of the system Solvent bulk length Membrane length Permeate bulk length

i. **Effect of time**

Initial concentration $c_{Na^+,\infty} = 0.5M$ $c_{Cl^-,\infty} = 0.5M$	Debye length λ_D= 13.43 nm
Fixed charge density ζ_{fix}= -3	

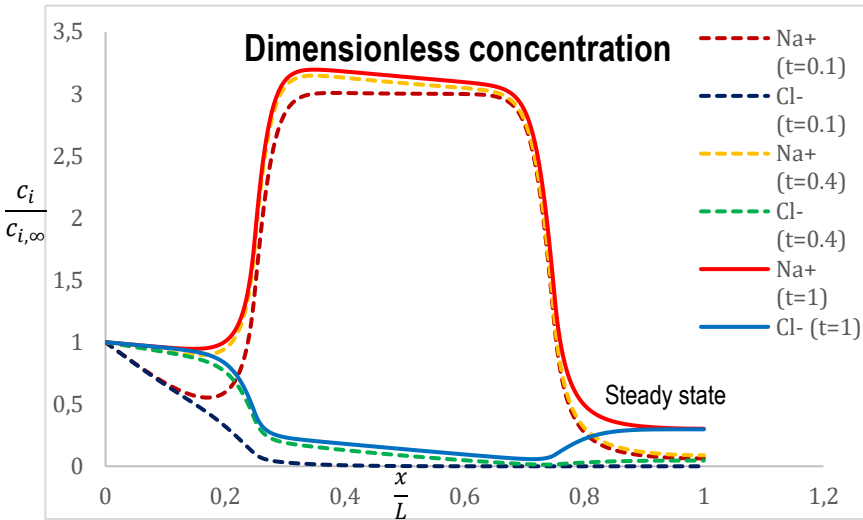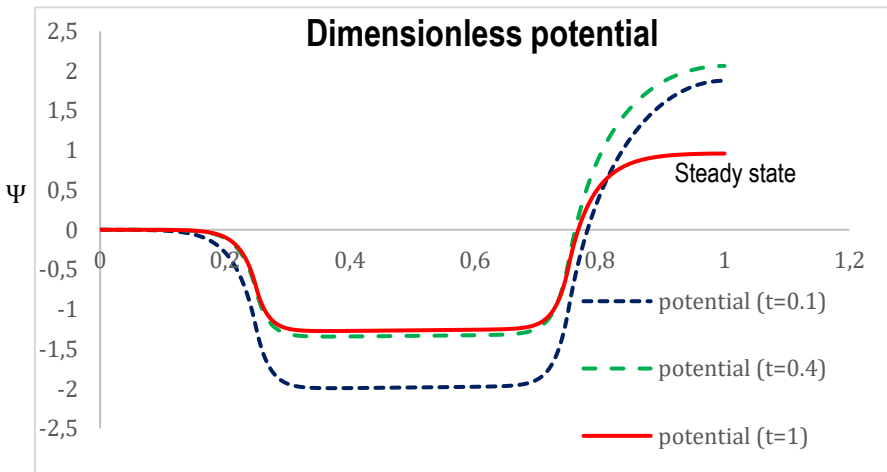Figure 23. Profiles of dimensionless ion concentration for different dimensionless times.

Figure 24. Profiles of dimensionless electrical potential for different dimensionless times.

In the figure 19. can be seen that the co-ions (Cl^-) decreases very fast, because the surface charge membrane makes a barrier of same charge, also in the first times, the co-ions and counter-ions they are attracted to each other in the boundary.

But in the steady state the profiles stabilized making a state of pseudo equilibrium in the interface, the Donnan equilibrium, because the counter-ions are accumulated at the interface membrane attracting the co-ions resulting a constant gradient of ions.

In the electrical potential can be seen that the potential increases in the right of the membrane, because the ions concentration decreases.

These systems are dynamically very fast, reaching the steady state very fast.

ii.   Effect of initial concentration

Initial concentration	Debye length
$c_{Na^+,\infty} = 3M$ $c_{Cl^-,\infty} = 3\ M$	λ_D= 5.5 nm
$c_{Na^+,\infty} = 0.5M$ $c_{Cl^-,\infty} = 0.5M$	λ_D= 13.43 nm
$c_{Na^+,\infty} = 0.05M$ $c_{Cl^-,\infty} = 0.05M$	λ_D= 42.5 nm
Fixed charge density ζ_{fix}= -1	

The initial concentration is an important variable, because the ionic force is dependant of it and the Debye length increase or decreases according to the ionic force.
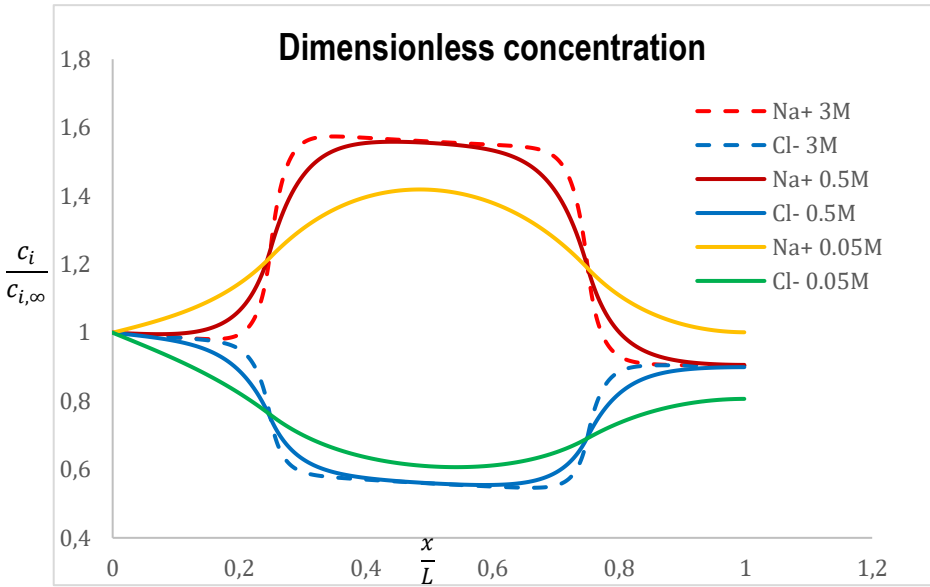
Figure 25. Profiles of dimensionless ion concentration for initial concentration or ionic strength.
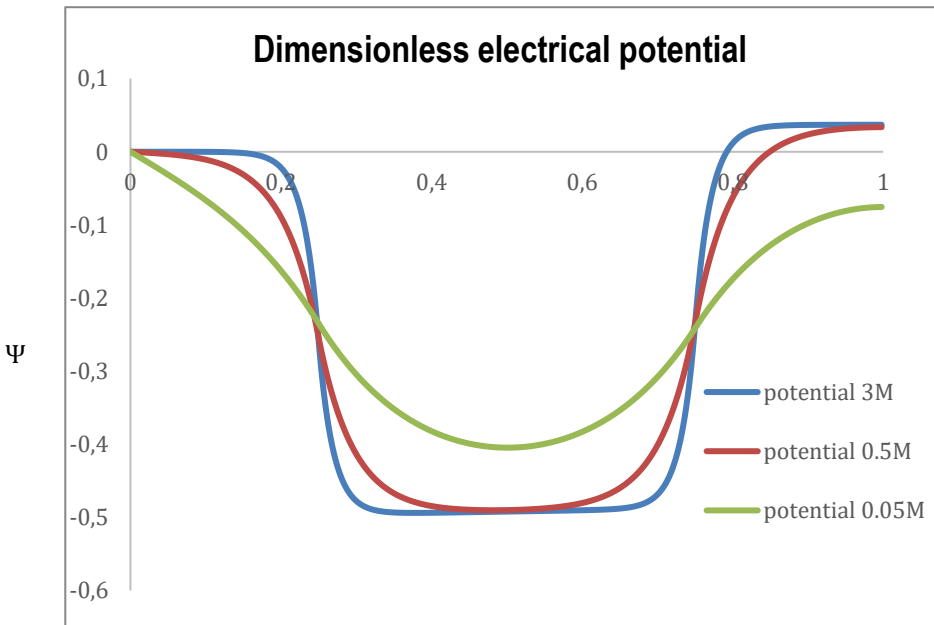
Figure 26. Profiles of dimensionless ion concentration with different initial concentration or ionic strength.

Can be seen that the initial concentration of the bulk makes crucial the behaviour of the ions in the membrane, if the initial concentration is high, then the ionic strength becomes high making the Debye length very small, because the counter ions are very attracted to the membrane. This also can be viewed with the electrical potential, that when the ionic strength increases the electrical potential also increases.

iii.   Effect of fixed charge density membrane

Initial concentration $c_{Na^+,\infty} = 0.5M$ $c_{Cl^-,\infty} = 0.5M$	Debye length λ_D = 13.43 nm
Fixed charge density ζ_{fix} = -0.1 ζ_{fix} = -1 ζ_{fix} = -2	
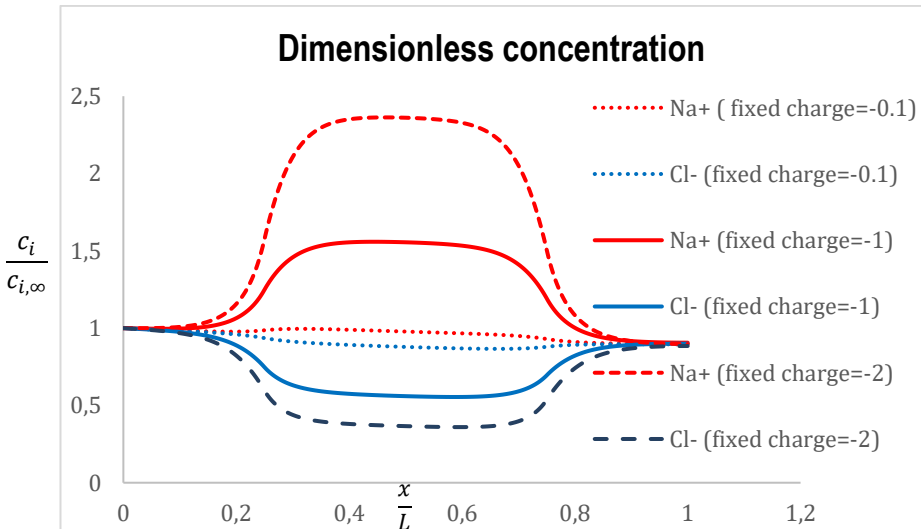
Figure 27. Profiles of dimensionless ion concentration with different fixed density charge of membrane.
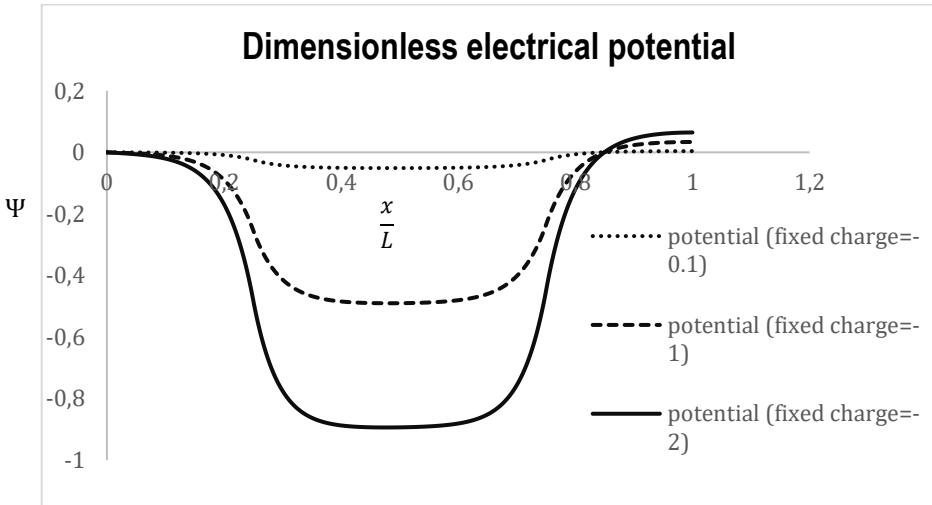
Figure 28. Profiles of dimensionless ion concentration with different fixed density charge of membrane.

The numerical solution also gives good physical significance with the dependence of the fixed charge of the membrane, when the fixed charges decreases, in the membrane the concentration of co-ions decreases significantly, and the counter-ions becomes very high. Also, the electrical potential is proportional to the fixed charge density, note that when the electrical potential becomes very negative, the concentration of counter-ions increases significantly.

iv.   Effect of velocity

Initial concentration $c_{Na^+,\infty} = 0.5M$ $c_{Cl^-,\infty} = 0.5M$	Debye length λ_D = 13.43 nm
Fixed charge density ζ_{fix} = -1	T= 293.15 K
Velocity u = 0.03 m/s u = 0.5 m/s u = 2 m/s	
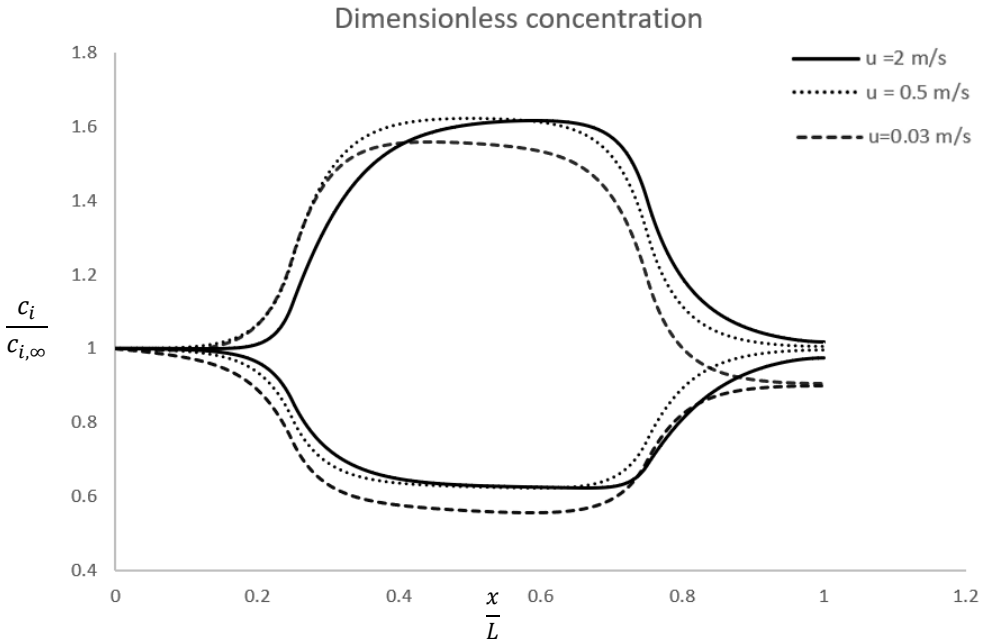
Figure 29. Profiles of dimensionless ion concentration with different fluid flow velocity.

In the graphic can be seen that when the velocity increases, in the membrane the co-ions concentration descreases and increases in the case of counter-ions. Also, the curves becomes asymmetric when the velocity increases, this is because the increment of flux pushes the ions towards the membrane causing the convective flow to exceed the electrical forces.

Also, can be viewed that the final concentration increases because the flow drags the ions to the outside of the membrane making the permeate more concentrated in ions.

v.   Effect of Temperature

Initial concentration $c_{Na^+,\infty} = 0.5M$ $c_{Cl^-,\infty} = 0.5M$	Debye length λ_D = 13.43 nm		
Fixed charge density ζ_{fix} = -2	Temperature T = 293 K	λ_D = 13.43 nm	
	T =350 K	λ_D = 14.73 nm	
	T = 600 K	λ_D = 19.3 nm	

Figure 30. Profiles of dimensionless ion concentration with different temperature.

For visualize the effect of temperature is better to plot the profile concentration from the bulk to the interface of membrane (x/L = 0.25).
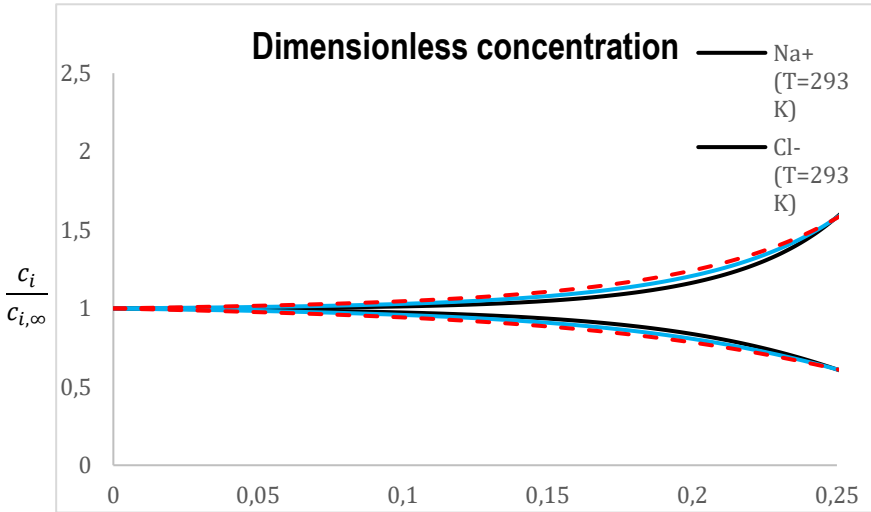
Figure 31. Profiles of dimensionless ion concentration from the bulk to the membrane interface with different temperature.
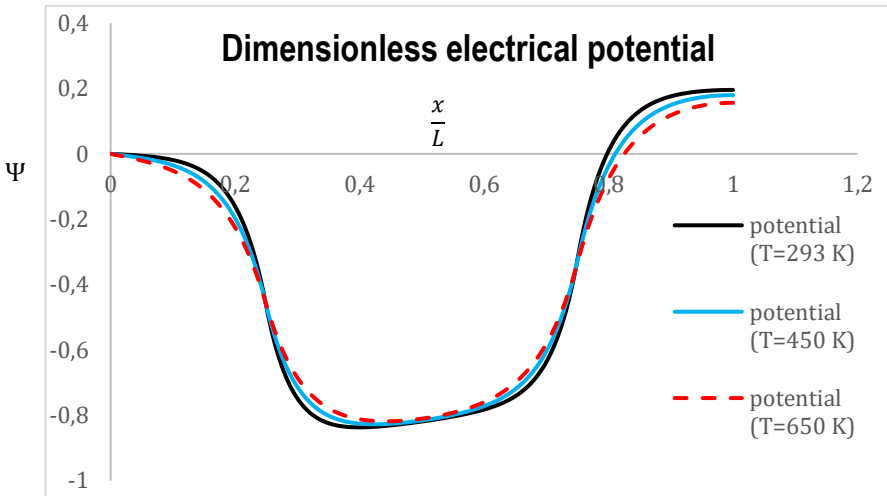
Figure 32. Profiles of dimensionless ion concentration from the bulk to the membrane interface with different temperature.

The temperature is also a decisive variable in this kind of systems, because the length of the electrical double layer depends on it. When the temperature increases the thermal energy

increases, so the diffusive layer spreads, in other words, the diffusion of the ions exceed the electrostatic forces making the Debye length bigger. This can be seen with the Einstein relation:

$$D_i = M_i R\, T$$

With the Einstein relation this is more clearly, when the Temperature increases the brownian motion increases making the diffusivity larger.

In the case of potential, can be explained by the section 1.2.2.1 Low potential approximation, in the potential plots can be seen that when the temperature increases the electrical double layer also increases making the electrical potential smaller, this is because the thermal energy produced by the brownian motion exceed the electrical potential energy.

vi.   Effect of steric coefficient

Initial concentration $c_{Na^+,\infty} = 0.5M$ $c_{Cl^-,\infty} = 0.5M$	Debye length λ_D = 13.43 nm
Fixed charge density ζ_{fix} = -2	Steric coefficient $g_{ij} = 0$ $g_{ij} = 0.05$ $g_{ij} = 0.5$
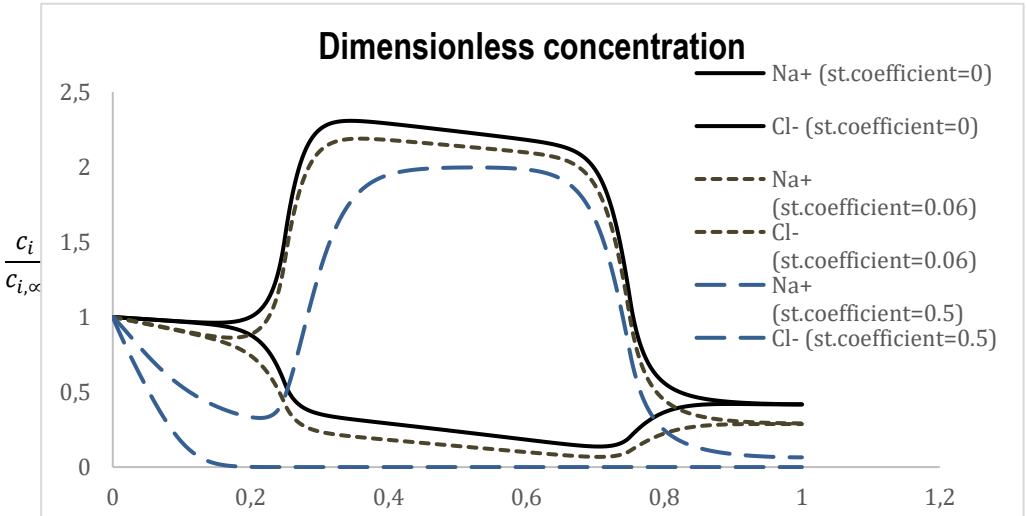
Figure 33. Profiles of dimensionless ion concentration with steric coefficient.

In this graphic can be observed that the steric effect is crucial for the exclusion of the ions in the membrane, the classic Nernst-Planck equations are able to predict in a general way the ions behaviour but not with exactitude to describe the exclusion. When the Nernst-Planck equations include the steric effects, the exclusion of the ions became very high like in the real systems of membranes.

This reason is because the NP equations are general for predict transport of ions in dilute solutions and in cases where the pore radius don't have a crucial decision in the exclusion of ions, but in the case of NF membranes the pore radius is very important, and the interactions of ion-ion also have a very important role, so including the steric effects in the NP equations can predict with more exactitude this complex systems with continuum models and making it unnecessary to resort to statistical physics and molecular dynamics simulations

5. CONCLUSIONS

After the validation of the model and the discussion of the effect of the variables that depend our system, can be concluded that the numerical method developed accomplish the objective: "**The main objective of the work is to propose a model of ion transport in a generalized way and solve it with the minimum of simplifications**".

The model has physical consistency, because all the numerical solutions ratify the double-layer theory of Gouy-Chapman. Also, the numerical solution is compared with a more complex model in 2D that also includes the Navier-Stokes equations, so if our model predict with exactitude the results of more complex models, ratify that the model of this project is very versatile giving good results with less computation resources.

Also is compared with a model that have very acceptance for predict the permeate concentration in the membrane engineering, the DSPM-DE model. The results of this work predict with exactitude the results of DPM-DE model.

So if the model is able to predict the behaviour of the ions inside the membrane and also the final concentration of the ions for a type of membrane, can be concluded that our model is useful to describe the concentration of ions for a given membrane and for designing membrane processes.

To finish, the effect of the variables is confirmed that the model is stable and meets its expectations, but in the case of classical Nernst-Planck equations they are not able to predict with absolute accuracy the exclusion of the ions, but including the steric term in the partial differential equations gives them the accuracy that they lack, so the steric effects are crucial to determine the selectivity of the membrane making extremely important to take into account.

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ACRONYMS

DAE   Differential algebraic equations

LEH   Local Equilibrium Hypothesis

MF   Microfiltration

NF   Nanofiltration

ODE   Ordinary differential equation

OHP   Outer Helmholtz Plane

PDE   Partial Differential equation

PNP   Poisson Nernst Planck

RO   Reverse osmosis

SC   Space charge model

TMS   Teorell Meyer Sievers

UF   Ultrafiltration

N_A	Avogadro's number
K_b	Boltzmann's constant
ΔW_i	Born energy solvation
$\partial\Omega$	Boundary
$D_{i,\infty}$	Bulk diffusivity
ε_b	Bulk permittivity
η_o	Bulk viscosity
C	Capacitance
μ_i	Chemical potential
c_{Cl^-}	Chloride concentration
D_{Cl^-}	Chloride diffusivity
z_{Cl^-}	Chloride valence
$c_{i,\infty}$	Concentration bulk of the ion
c_i	Concentration of the ion
$K_{i,c}$	Convective hindrance coefficient

λ_D	Debye's length
κ	Debye-Hückel parameter
$K_{i,D}$	Diffusion hindrance coefficient
$D_{i,p}$	Diffusivity at the pore membrane
D_i	Diffusivity of the ion
θ	Dimensionless concentration
$\tilde{\lambda}_D^2$	Dimensionless Debye length
Ψ	Dimensionless electrical potential
ζ_{fix}	Dimensionless fixed charge density
ξ	Dimensionless length scale
φ_{steric}	Dimensionless steric partition coefficient
$\Delta\psi_D$	Donnan potential
ψ	Electrical potential
E	Electrical field
$\tilde{\mu}_i$	Electrochemical potential
e	Electron mass
F	Faraday's constant
ρ_{fix}	Fixed charge density of the membrane
G	Gibbs energy
r_i	Ionic radius
I	Ionic strength
ϑ	Kinematic viscosity
Ω_m	Membrane region
δ^+	Membrane thickness
M_i	Mobility of the ion
F_i	Molar flux
$\omega\,\epsilon_{ij}$	Molecular steric coefficients
Pe	Peclet number
$C_{i,p}$	Permeate concentration
Ω_p	Permeate region
ε_r	Permittivity of the solvent
ε_o	Permittivity of vacuum
ε_p	Pore permittivity
r_p	Pore radius
η	Pore viscosity
P	Pressure
λ_i	Ratio of the ionic radius by the pore radius
c_{Na^+}	Sodium concentration
D_{Na^+}	Sodium diffusivity

z_{Na^+}	Sodium valence
$C_{i,s}$	Solvent concentration
Ω_s	Solvent region
g_{ij}	Steric coefficient
σ	Surface charge density
R	Universal gas constant
z_i	Valence of the ion
u	Velocity
ρ_i	Volumetric charge density

APPENDICES

APPENDIX 1: MATHEMATICAL METHOD

The method of finite difference can be defined by the standard definition of the derivative:

$$f'(x) = \lim_{h \to \infty} \frac{f(h + x_i) - f(x_i)}{h}$$

And can be approximated to

$$f'(x)_{approx} = \frac{f(h + x_i) - f(x_i)}{h}$$

But a definition for the difference formula by the Taylor expansion

$$f(x_{i+1}) = f(x_i) + h\,f'(x_i) + \frac{h^2}{2}f''(\xi_i); \; x_i < \xi_i < x_{i+1}$$

Which is more useful because the error can be estimated:

$$f'(x_i) = \frac{f(x_{i+1}) - f(x_i)}{h} - \frac{h^2}{2}f''(\xi_i)$$

It is important to think that ξ_i must lie between x_{i+1} and x_i because the error is local. Typically, the error is expressed in asymptotic form:

$$f'(x_i) = \frac{f(x_{i+1}) - f(x_i)}{h} + O(h)$$

This finite difference formula is referred to first-order forward difference, the backward difference the interval used lie between x_i and x_{i-1}.

Taylor expansions can be used to derive high-order approximations. For example:

$$f(x_{i+1}) = f(x_i) + h\,f'(x_i) + \frac{h^2}{2}f''(x_i) + O(h^3)$$

And

$$f(x_{i-1}) = f(x_i) + h\,f'(x_i) + \frac{h^2}{2}f''(x_i) + O(h^3)$$

Solving for $f'(x_i)$ gives the second-order centered difference formula for the first derivative

$$f'(x_i) = \frac{f(x_{i+1}) - f(x_{i-1})}{2h} + O(h^2)$$

And the second order centred difference formula for the second derivative

$$f''(x_i) = \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{h^2} + O(h^2)$$

Mathematica provided a kernel function with the Fonberg algorithm that is not difficult to implement in Mathematica. Finite differences have been implemented through a data object that allows efficient evaluation of finite differences over an entire grid given a vector representing the function values on the grid.

When the data object is constructed for a derivative and grid, finite difference weights are computed using the fast and accurate weight computation algorithm of Fonberg and formed into a (sparse) differentiation matrix that the data object stores. The weight generation algorithm makes it easy to support uniform or non-uniform grids along with an arbitrary approximation order of finite difference. The approximation order can be specified by an option. The default of 4th order differences was chosen because for a large class of functions you can use far fewer spatial points and still get a better approximation than with second order differences, but going to higher order can increase both roundoff error and implicit solving complexity without as much decrease in the number of spatial points. Boundaries are handled by one-sided derivative approximations. An easy way to see the formulas that are being used is to give symbolic function values [18]. For example, on a uniform grid with spacing h = 1 with 4 grid points the first derivative approximated with finite difference method with difference order 4 is

```
In[23]:= npts = 4;
        uu = Table[u_i, {i, 0, npts}];
        fdd = NDSolve`FiniteDifferenceDerivative[1, Range[0, npts], uu, DifferenceOrder → 4];
        diff = Thread[Table[u'_i, {i, 0, npts}] == fdd];
        MatrixForm[diff]
```

$$
\begin{pmatrix}
(u')_0 == -\frac{25u_0}{12} + 4u_1 - 3u_2 + \frac{4u_3}{3} - \frac{u_4}{4} \\
(u')_1 == -\frac{u_0}{4} - \frac{5u_1}{6} + \frac{3u_2}{2} - \frac{u_3}{2} + \frac{u_4}{12} \\
(u')_2 == \frac{u_0}{12} - \frac{2u_1}{3} + \frac{2u_3}{3} - \frac{u_4}{12} \\
(u')_3 == -\frac{u_0}{12} + \frac{u_1}{2} - \frac{3u_2}{2} + \frac{5u_3}{6} + \frac{u_4}{4} \\
(u')_4 == \frac{u_0}{4} - \frac{4u_1}{3} + 3u_2 - 4u_3 + \frac{25u_4}{12}
\end{pmatrix}
$$

The function that the finite difference derivative is applied

The grid that the derivative is evaluated

```
Thread[f[args]]
In[1]:= Thread[f[{a, b, c}]]
Out[1]= {f[a], f[b], f[c]}
```

Derivative order who has to be discretized

Is the Matrix form of the discretized first derivative of the function on the grid with 4th order Taylor series. Here is a table to present the kernel function of the finite difference method used:

`NDSolve`FiniteDifferenceDerivative[Derivative[m], grid, values]`	approximate the mth-order derivative for the function that takes on values on the grid
`NDSolve`FiniteDifferenceDerivative[` `Derivative[m_1, m_2, ..., m_n], {grid_1, grid_2, ..., gridn}, values]`	approximate the partial derivative of order $(m_1, m_2, ..., m_n)$ for the function of n variables that takes on values on the tensor product grid defined by the outer product of $(grid_1, grid_2, ..., grid_n)$
`NDSolve`FiniteDifferenceDerivative[Derivative[m_1, m_2, ..., m_n], {grid_1, grid_2, ..., gridn}]`	compute the finite difference weights needed to approximate the partial derivative of order $(m_1, m_2, ..., m_n)$ for the function of n variables on the tensor product grid defined by the outer product of $(grid_1, grid_2, ..., grid_n)$; the result is returned as an `NDSolve`FiniteDifferenceDerivativeFunction`, which can be repeatedly applied to values on the grid

Figure 1. Description of the finite difference algorithm by Wolfram Mathematica.

Typically, when computing a PDE solution, it is common to repeat the same finite difference scheme to different values or function on the same grid. For this reason, Mathematica gives a kernel function with the same finite difference algorithm but does not require to specify the function or values on the grid, by this way can be used the algorithm for different values. In the

last table can be seen that in the Mathematica function the third argument are the function values, when you omit this argument the result will be an NDSolve FiniteDifferenceDerivative Function, which is the finite difference weights stored in an efficient form for future use.

For example, suppose you have values of the sine function on a grid with uniform spacing between 0 and 2π.

Example by Knapp.R "A Method of Lines Framework in Mathematica." Journal of Numerical Analysis, Industrial and Applied Mathematics, 2007.

$$\text{grid} = (2.\pi/20)\text{Range}[0, 20];$$
$$\text{values} = \text{Sin}[\text{grid}];$$

Then, constructing a FiniteDifferenceDerivative object on the grid for the first derivative returns a function that optimizes finite difference approximation.

$$\text{fder} = \text{NDSolveFiniteDifferenceDerivative}[\text{Derivative}[1], \text{grid}]$$

$$\text{NDSolveFiniteDifferenceDerivativeFunction}[\text{Derivative}[1], <>]$$

The function can be applied to the vector of values to get the vector of derivative values as shown in figure

$$\text{ListPlot}[\{\text{values}, \text{fder}[\text{values}]\}, \text{DataRange} \to \{0, 2\pi\}, \text{PlotMarkers} \to \text{Automatic}].$$
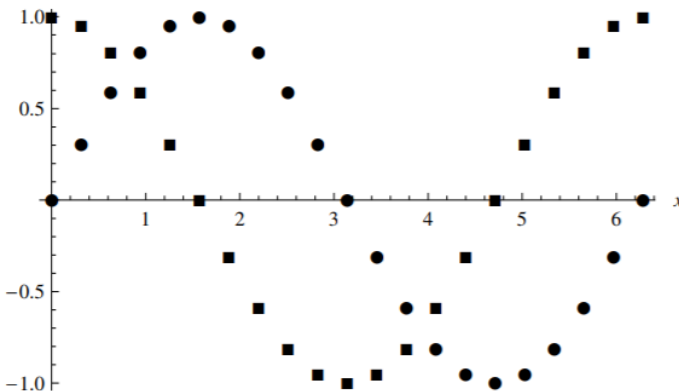

Figure 2. Plot of the function Sin[x] and his derivative.

Where the circles are the values of the function and the squares are the first derivative of the values.

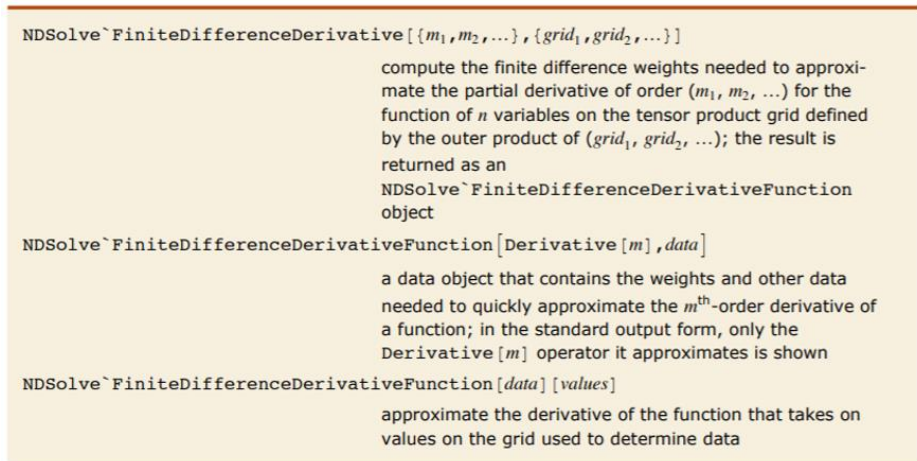The information of this method from Mathematica is

Figure 3. Description of the finite difference algorithm by Wolfram Mathematica.

When the derivatives are discretized with this algorithm the result is a system of ODEs or DAEs with temporal derivatives. If the refinement of the grid is high, the number of grid points becomes very high and the system of ODEs or DAEs becomes very large. For represent the finite differences weights in large systems is convenient to express the finite difference weights with Differentiation Matrix.

Finite difference approximation is a linear operation, the alternative to express FiniteDifferenceDerivative Function is with a matrix. Differentiation matrices are not always the best way but in finite difference approximations can be used to reduce complexity and error.

For illustrate the Differentiation Matrix is discretized with second-order centred difference formula for the first derivative and the second-order one-sided difference are required at the boundaries

$$u'_i = \frac{u_{i+1} - u_i}{2h} + O(h^2)$$

$$u'_i = \frac{-3\,u_i + 4\,u_{i+1} - u_{i+2}}{2h} + O(h^2)$$

$$u'_i = \frac{u_{i-2} - 4\,u_{i-1} + 3\,u_i}{2h} + O(h^2)$$

For i=1,...N, be a grid of equally spaced points [0,1] where h= 1/(N-1)

Using the finite difference formula, the first derivative values can be approximated by

$$u'_i = D\,u_i$$

Where D is a NxN differentiation matrix

$$D = \frac{1}{h}\begin{bmatrix} -3/2 & 2 & -1/2 & & & & \\ -1/2 & 0 & 1/2 & & & & \\ & -1/2 & 0 & 1/2 & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & -1/2 & 0 & 1/2 \\ & & & 1/2 & -2 & 3/2 \end{bmatrix}$$

With the Mathematica algorithm has the next form

```
npts = 10
nx = Range[0, 1, 1/(npts - 1)];
```

Define the grid nx for i=0,...1 equally spaced with h =1 /(npts-1)

```
In[3]:= fdd = NDSolve`FiniteDifferenceDerivative[1, nx, DifferenceOrder → 2]

Out[3]= NDSolve`FiniteDifferenceDerivativeFunction[Derivative[1], <>]
```

Apply the finite difference algorithm for a first derivative approximated to second order Taylor.

And we apply the kernel function Differentiation Matrix to get the matrix defined before

```
In[4]:= smat = fdd["DifferentiationMatrix"];
        MatrixForm[smat / (npts - 1)]
```

Differentiation matrix of the first derivative approximated to second order Taylor

Out[5]//MatrixForm=

N

If we do the product $D\ u_i$ result

$$u'_i = D\ u_i$$

```
In[13]:= MatrixForm [smat.uu] ;
         diff = Thread[Table[u'ᵢ, {i, 0, npts}] == smat.uu];
         MatrixForm[diff]
```
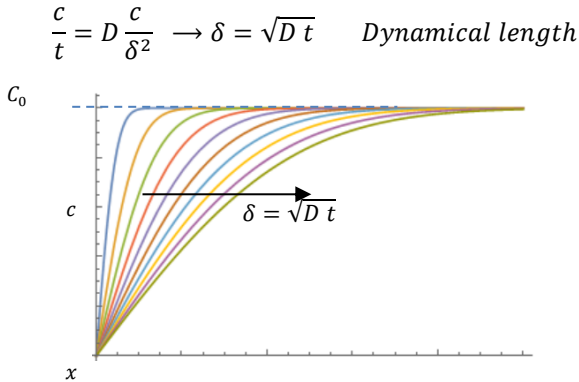
Out[15]//MatrixForm=

$$
\begin{pmatrix}
u'_0 = -\dfrac{3\,u_0}{2} + 2\,u_1 - \dfrac{u_2}{2} \\[6pt]
u'_1 = -\dfrac{u_0}{2} + \dfrac{u_2}{2} \\[6pt]
u'_2 = -\dfrac{u_1}{2} + \dfrac{u_3}{2} \\[6pt]
u'_3 = -\dfrac{u_2}{2} + \dfrac{u_4}{2} \\[6pt]
u'_4 = -\dfrac{u_3}{2} + \dfrac{u_5}{2} \\[6pt]
u'_5 = -\dfrac{u_4}{2} + \dfrac{u_6}{2} \\[6pt]
u'_6 = -\dfrac{u_5}{2} + \dfrac{u_7}{2} \\[6pt]
u'_7 = -\dfrac{u_6}{2} + \dfrac{u_8}{2} \\[6pt]
u'_8 = -\dfrac{u_7}{2} + \dfrac{u_9}{2} \\[6pt]
u'_9 = -\dfrac{u_8}{2} + \dfrac{u_{10}}{2} \\[6pt]
u'_{10} = \dfrac{u_8}{2} - 2\,u_9 + \dfrac{3\,u_{10}}{2}
\end{pmatrix}
$$

Before starting to implement the Line Method algorithm to solve the system of PNP equations. it will solve PDEs that have analytical solution and verify that the numeric method works correctly.

The basic example of PDE is the classical diffusion equation that have analytical solution in semi-infinite and infinite regions. The first example is a diffusion process in a semi-infinite regions with the following conditions.

$$\frac{\partial c(x,t)}{\partial t} = D\,\frac{\partial^2 c(x,t)}{\partial x^2} \quad ; 0 < x < \infty$$
$$IC: c(x,0) = C_0$$
$$BC: c(0,t) = 0$$
$$BC: c(\infty,t) = C_0$$

Scaling the equation

$$\frac{c}{t} = D \frac{c}{\delta^2} \rightarrow \delta = \sqrt{D\,t} \qquad Dynamical\ length$$

With the dynamical length can be defined a non-dimensional variable that involves the two-dimensional independent variable (similarity variable)

$$\xi = \frac{x}{\delta} = \frac{x}{\sqrt{D\,t}}$$

The solution c(x,t) will be the form

$$c(x,t) = C_0 F\left(\frac{x}{2\sqrt{D\,t}}\right)$$

And the dimensionless concentration

$$\theta = \frac{c(x,t)}{C_0} = F\left(\frac{x}{2\sqrt{D\,t}}\right)$$

Considerations

$$\frac{\partial \xi}{\partial t} = \left(\frac{x}{2\sqrt{D}}\right)\left(-\frac{1}{2}t^{-\frac{3}{2}}\right) = \left(\frac{x}{2\sqrt{D}}\,t^{-\frac{1}{2}}\right)\left(-\frac{1}{2}t\right)$$

$$\frac{\partial \xi}{\partial t} = -\frac{\xi}{2t}$$

$$\frac{\partial \xi}{\partial x} = \frac{1}{2\sqrt{Dt}}$$

For the rule of change of variables and make the concentration dimensionless gives

$$\frac{\partial \xi}{\partial t}\frac{\partial \theta C_0}{\partial \xi} = \frac{\partial}{\partial x}\left(\frac{\partial \xi}{\partial x}\frac{\partial \theta C_0}{\partial \xi}\right)$$

With the considerations and the equation gives

$$\frac{d^2\theta}{d\xi^2} + 2\xi \frac{\partial\theta}{\partial\xi} = 0$$

Reconsidering the conditions with the similarity variable

$$IC: \theta(x,0) = 1 \rightarrow \theta\left(\frac{x}{0}\right) = \theta(\infty) = 1$$

$$BC: \theta(0,t) = 0 \rightarrow \theta\left(\frac{0}{2\sqrt{Dt}}\right) = 0$$

$$BC: \theta(\infty,t) = 1 \rightarrow \theta(\infty) = 1$$

We can see that the initial condition and the infinite boundary condition with this new formulation becomes the same, this method is called similarity variable and can be used with that cases when many conditions becomes the same and the equation can be simplified to an ODE.

Introducing the new notation to the PDE gives

$$\theta = \frac{c(x,t)}{C_0} = F\left(\frac{x}{2\sqrt{D\,t}}\right)$$

$$\frac{d^2\theta}{d\xi^2} + 2\xi \frac{d\theta}{d\xi} = 0$$

$$\frac{d^2F(\xi)}{d\xi^2} + 2\xi \frac{dF(\xi)}{d\xi} = 0$$

Introducing the integrator factor

$$\frac{d^2F(\xi)}{d\xi^2} + 2\xi \frac{dF(\xi)}{d\xi} = \frac{d}{d\xi}\left(e^{\xi^2} \frac{dF(\xi)}{d\xi}\right) = 0$$

Note that integrating factor is to be able to integrate the ODE, integrating the equation gives

$$e^{\xi^2} \frac{dF(\xi)}{d\xi} = A$$

$$dF(\xi) = Ae^{-\xi^2} d\xi$$

Integrating the equation and apply the boundary condition

$$F(\xi) = \int_0^\xi A e^{-s^2} ds$$

$$F(\infty) = \int_0^\infty A e^{-s^2} ds = 1 = A \frac{\sqrt{\pi}}{2} = 1$$

$$A = \frac{\sqrt{\pi}}{2}$$

Giving the solution of the equation

$$F(\xi) = \frac{\sqrt{\pi}}{2} \underbrace{\int_0^\xi e^{-s^2} ds}_{\text{Error function}} = \frac{\sqrt{\pi}}{2} \operatorname{erf}(\xi)$$

$$c(x,t) = C_0 \frac{\sqrt{\pi}}{2} \operatorname{erf}(\frac{x}{2\sqrt{D\,t}})$$

For solve this PDE with the Method Of Lines in Mathematica code have the following form:
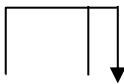
First of all, the grid must be defined

```
In[1]:= npts = 100;
        nx = Range[0, 1, 1/(npts - 1)];
```

nx for i=0,...1 equally spaced with h =1 /(npts-1). The next step is to implement the finite difference algorithm in the grid to approximate the second spatial derivative of the PDE in a differentiation matrix

The second derivative approximation is called d2x2 and is approximated with a second difference order in a differentiation matrix like the before examples.

```
In[3]:= d2dx2 = NDSolve`FiniteDifferenceDerivative[Derivative[2], nx, "DifferenceOrder" -> 2]["DifferentiationMatrix"];
```

The dimensionless diffusion equation in Mathematica has the following form

```
In[4]:= u = Array[uu[#][t] &, npts];
        eqn1 = Thread[D[u, t] == d2dx2.u];
```

For define the function u[x,t] an Array has used, but in this case de spatial variable is discrete because the finite difference method is used, and the temporal variable is continuous . For this reason the Array defined is a vector that depend on [nx=grid] and [t] and the simplest way to implement it is to use an Array function.

The definition of an Array in Mathematica is

Array[f, n]

    generates a list of length *n*, with elements $f[i]$.

Example:

In[1]:= Array[f, 10]

Out[1]= {f[1], f[2], f[3], f[4], f[5], f[6], f[7], f[8], f[9], f[10]}

But for define an Array that depends on two variable and one of them is continuos, (temporal variable because is not defined a grid for the time), is to use the # notation. The # notation in Mathematica is to represent an argument defined by &,*(object)*. Example:

(1 + #) &[x]

1 + x

The result of this Array on the function is :

u = Array[uu[#][t] &, npts]

{uu[1][t], uu[2][t], uu[3][t], uu[4][t], uu[5][t], uu[6][t], uu[7][t], uu[8][t], uu[9][t], uu[10][t], uu[11][t], uu[12][t], uu[13][t], uu[14][t], uu[15][t], uu[16][t], uu[17][t], uu[18][t], uu[19][t], uu[20][t], uu[21][t], uu[22][t], uu[23][t], uu[24][t], uu[25][t], uu[26][t], uu[27][t], uu[28][t], uu[29][t], uu[30][t], uu[31][t], uu[32][t], uu[33][t], uu[34][t], uu[35][t], uu[36][t], uu[37][t], uu[38][t], uu[39][t], uu[40][t], uu[41][t], uu[42][t], uu[43][t], uu[44][t], uu[45][t], uu[46][t], uu[47][t], uu[48][t], uu[49][t], uu[50][t], uu[51][t], uu[52][t], uu[53][t], uu[54][t], uu[55][t], uu[56][t], uu[57][t], uu[58][t], uu[59][t], uu[60][t], uu[61][t], uu[62][t], uu[63][t], uu[64][t], uu[65][t], uu[66][t], uu[67][t], uu[68][t], uu[69][t], uu[70][t], uu[71][t], uu[72][t], uu[73][t], uu[74][t], uu[75][t], uu[76][t], uu[77][t], uu[78][t], uu[79][t], uu[80][t], uu[81][t], uu[82][t], uu[83][t], uu[84][t], uu[85][t], uu[86][t], uu[87][t], uu[88][t], uu[89][t], uu[90][t], uu[91][t], uu[92][t], uu[93][t], uu[94][t], uu[95][t], uu[96][t], uu[97][t], uu[98][t], uu[99][t], uu[100][t]}

The boundary condition are declared with this form

In[6]:= eqn1[[1]] = u[[1]] == 0

    eqn1[[npts]] = u[[npts]] == 1

Out[6]= uu[1][t] == 0

Out[7]= uu[100][t] == 1

The [[n]] notation in Mathematica is a way to extract the "n" of a list, is an easy way to declare the value on the extremes of the grid.

The resulting system of DAEs with the boundary conditions are

$$uu[1][t] == 0$$
$$uu[2]'[t] == 9801\ uu[1][t] - 19602\ uu[2][t] + 9801\ uu[3][t]$$
$$uu[3]'[t] == 9801\ uu[2][t] - 19602\ uu[3][t] + 9801\ uu[4][t]$$
$$uu[4]'[t] == 9801\ uu[3][t] - 19602\ uu[4][t] + 9801\ uu[5][t]$$
$$uu[5]'[t] == 9801\ uu[4][t] - 19602\ uu[5][t] + 9801\ uu[6][t]$$
$$uu[6]'[t] == 9801\ uu[5][t] - 19602\ uu[6][t] + 9801\ uu[7][t]$$
$$uu[7]'[t] == 9801\ uu[6][t] - 19602\ uu[7][t] + 9801\ uu[8][t]$$
$$uu[8]'[t] == 9801\ uu[7][t] - 19602\ uu[8][t] + 9801\ uu[9][t]$$
$$uu[9]'[t] == 9801\ uu[8][t] - 19602\ uu[9][t] + 9801\ uu[10][t]$$
$$uu[10]'[t] == 9801\ uu[9][t] - 19602\ uu[10][t] + 9801\ uu[11][t]$$
$$uu[11]'[t] == 9801\ uu[10][t] - 19602\ uu[11][t] + 9801\ uu[12][t]$$
$$uu[12]'[t] == 9801\ uu[11][t] - 19602\ uu[12][t] + 9801\ uu[13][t]$$
$$uu[13]'[t] == 9801\ uu[12][t] - 19602\ uu[13][t] + 9801\ uu[14][t]$$
$$uu[14]'[t] == 9801\ uu[13][t] - 19602\ uu[14][t] + 9801\ uu[15][t]$$

$$\vdots$$

$$uu[96]'[t] == 9801\ uu[95][t] - 19602\ uu[96][t] + 9801\ uu[97][t]$$
$$uu[97]'[t] == 9801\ uu[96][t] - 19602\ uu[97][t] + 9801\ uu[98][t]$$
$$uu[98]'[t] == 9801\ uu[97][t] - 19602\ uu[98][t] + 9801\ uu[99][t]$$
$$uu[99]'[t] == 9801\ uu[98][t] - 19602\ uu[99][t] + 9801\ uu[100][t]$$
$$uu[100][t] == 1$$

The initial condition

```
In[8]:= ic1 = Thread[u == 1] /. t → 0;
```

And solve the system of DAEs with a NDSolve

```
In[9]:= vars = Flatten[u] /. x__[t] ⧴ x;
        PDEsol = First[NDSolve[{eqn1, ic1}, vars, {t, 0, 1}]];
```

The variable "vars" is used to can be solve the equation in NDSolve , because without this change of variable in NDSolve must be defined the variable "x" and "t" and the spatial variable was defined in the grid.

For view the concentration solution in the spatial direction we must be define a time scale. The solution is in dimensionless form, for this reason an initial concentration, diffusion coefficient , an axial longitude and a dimensional time must be defined.

Note: For compare the analytical solution and the numerical solution, the diffusion coefficient and the time scale must be small, because the analytical solution is in a semi-infinite region $[0,\infty]$ for this reason the comparison between the analytical and numerical solutions will be valid when the value $\frac{x}{2\sqrt{D\,t}}$ on the last point of the grid tends to infinity.

$$C_o = 0.5 \; \frac{mol}{m^3}$$
$$D = 0.25 \; \frac{m^2}{s}$$
$$t_1 = 0.05 \; s$$
$$t_2 = 0.15 \; s$$
$$t_3 = 0.25 \; s$$
$$t_3 = 0.5 \; s$$
$$L = 1 \; m$$

And the dimensionless time scale and the dimensionless concentration are

$$\tau \; \frac{t\,D}{L^2}$$
$$\theta = \frac{c}{C_o}$$

The numerical solution in Mathematica is dimensionless, for express the solution with the before conditions must be defined in dimensionless variables

```
Diff = 0.25; L = 1;
csol1 = (u /. t → 0.05 Diff / L^2) /. PDEsol;
uu1 = Interpolation[csol1];
csol2 = (u /. t → 0.15 Diff / L^2) /. PDEsol;
uu2 = Interpolation[csol2];
csol3 = (u /. t → 0.25 Diff / L^2) /. PDEsol;
uu3 = Interpolation[csol3];
csol4 = (u /. t → 0.5 Diff / L^2) /. PDEsol;
uu4 = Interpolation[csol4];
```

And the plot of the solution with the different time scales is
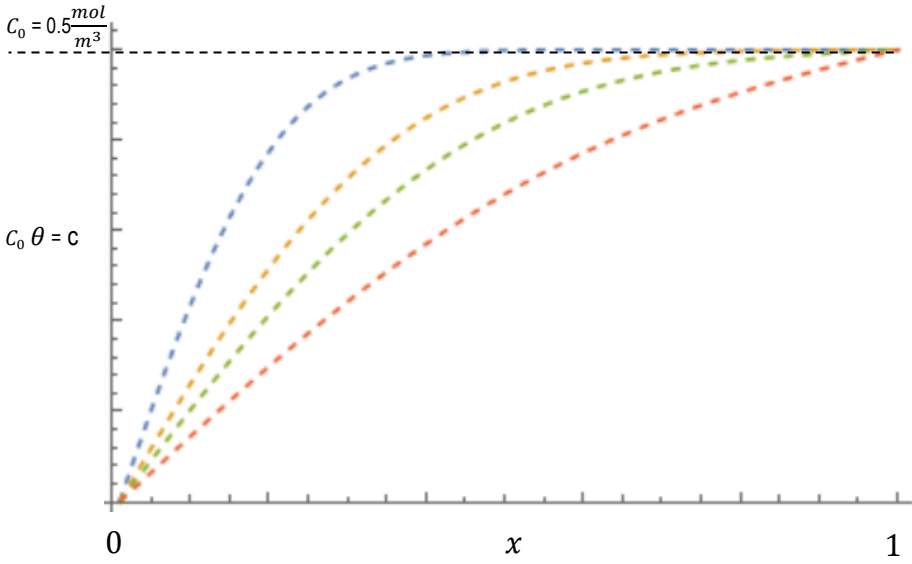
And the analytical solution with these conditions $c(x,t) = C_0 \frac{\sqrt{\pi}}{2} \mathrm{erf}(\frac{x}{2\sqrt{D\,t}})$
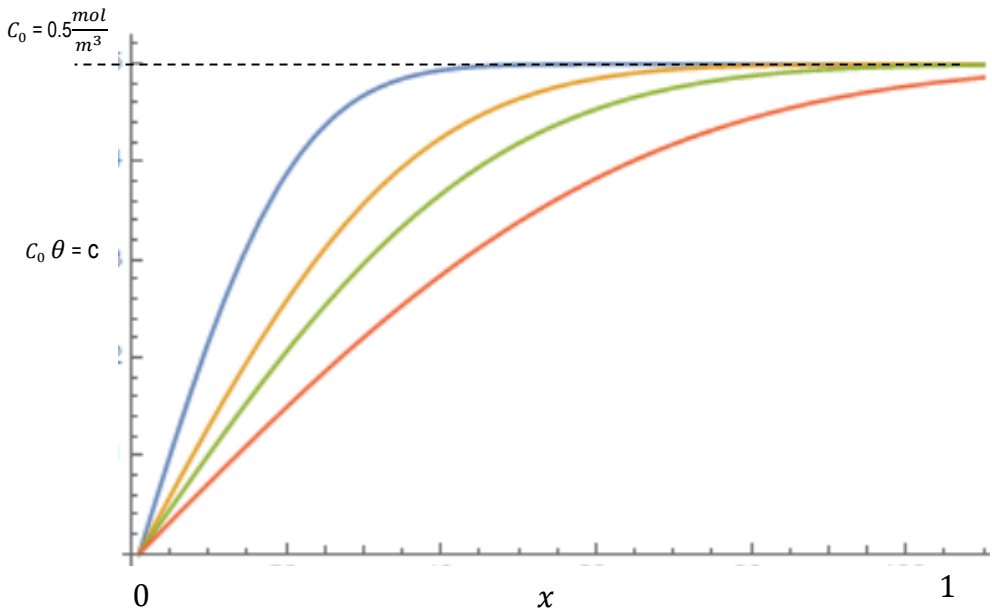
The comparison between them

$C_0 \, \theta = c$

0   x 1
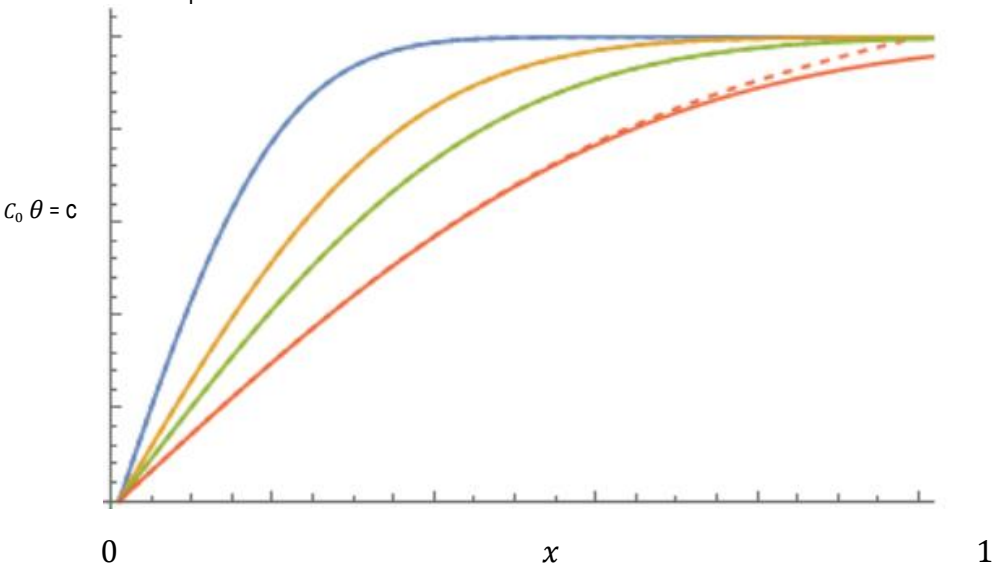
Can be concluded that the numerical solution is valid, but when the time scale becomes large in the red line when t=0.5 the semi-infinite analytical solution it needs more longitude to arrive to initial concentration.

The numerical method is also compared to the diffusion equation with a Neumann boundary condition for can be conclude that the method is consistent. For example, when the flux is specified in the begin of the domain:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2} \quad ; 0 < x < \infty$$
$$IC: c(x,0) = 0$$
$$BC: -D \frac{\partial c(0,t)}{\partial t} = f$$
$$BC: c(\infty, t) = 0$$

With the same method that the before PDE is solved this equation with these conditions gives:

$$c(x,t) = 2\sqrt{\frac{t}{D}}f\left(\frac{e^{-\xi^2}}{\sqrt{\pi}} - \xi\operatorname{erfc}\left(\frac{x}{2\sqrt{D\,t}}\right)\right)$$

Where $\operatorname{erf}c\left(\frac{x}{2\sqrt{D\,t}}\right) = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D\,t}}\right)$
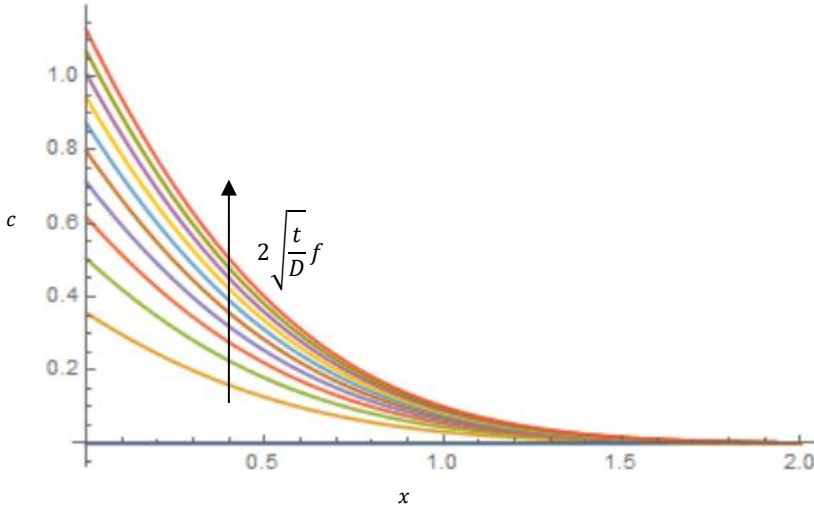
With the same procedure that the last example was solved in Mathematica, the numerical solution with these conditions gives

$$f = 0.5\,\frac{mol}{m^2 s}$$
$$D = 0.25\,\frac{m^2}{s}$$
$$t_1 = 0.05\ s$$
$$t_2 = 0.1\ s$$
$$t_3 = 0.2\ s$$
$$t_3 = 0.3\ s$$
$$L = 1\ m$$

x= n° points
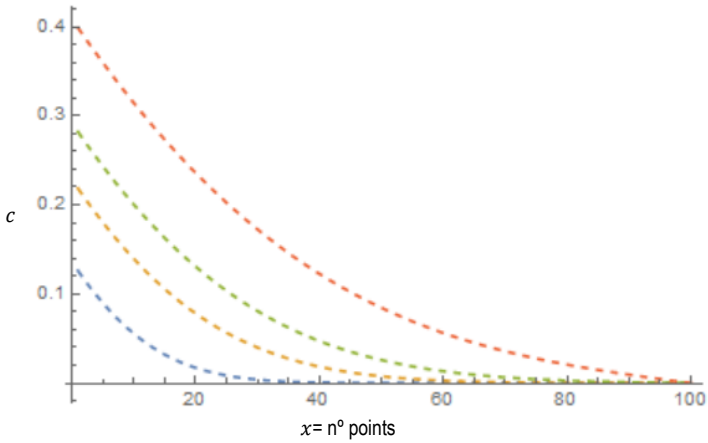
The comparison between the analytic solution is

x= n° points
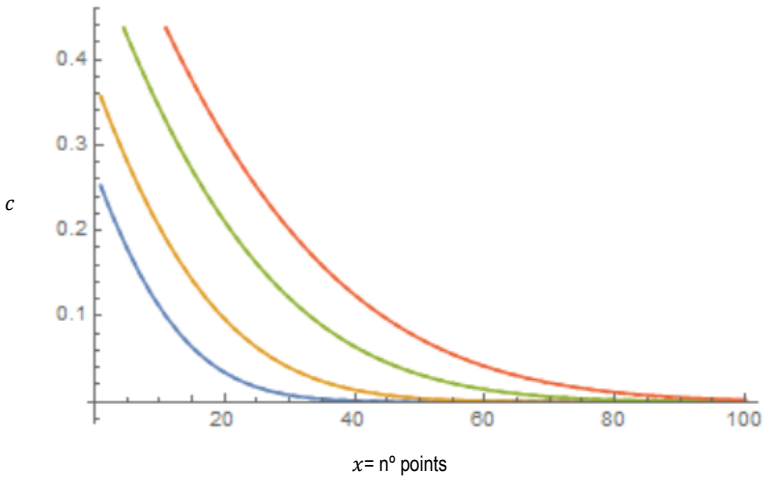
Can be concluded the numerical method is able to solve the diffusion equation with Dirichlet or Neumann boundary conditions.

APPENDIX 2: DIMENSIONAL ANALYSIS: BUCKINGHAM'S THEOREM

A quantity of interest is determined by n measurable quantities (the independent variables and parameters) $\{x1, x2, \ldots, xn\}$ as

$$\Omega = f\left(\omega_1{}^{\alpha 1}, \omega_2{}^{\alpha 2},, \ldots, \omega_n{}^{\alpha n}\right)$$

That is to say, we expect to be able to make the units of Ω by combining the parameters ωi, these parameters can be the density, viscosity, diffusion, etc. In summary, the parameters are dependent of fundamental units, and each parameter is raised to some power αi.

The fundamental units like time, length, temperature, etc. Are called f_j, where the index is for the jth fundamental unit that appears in the problem.

The number of fundamental units are represented by *k*. Another way of representing the units of Ω is by using those fundamental units:

$$\Omega = \left(f_1{}^{\beta 1}, f_2{}^{\beta 2},, \ldots, f_m{}^{\beta k}\right)$$

Where the βj are the powers of the fundamental units that make up the units of Ω. Since both equations are equal to the same thing, we can set them equal to each other:

$$\omega_1{}^{\alpha 1}, \omega_2{}^{\alpha 2}, \ldots, \omega_n{}^{\alpha n} = f_1{}^{\beta 1}, f_2{}^{\beta 2},, \ldots, f_m{}^{\beta k}$$

The parameters ωi has some units, so we can also represent them using the f_j :

$$[\omega] = f_1{}^{\gamma 1i} f_2{}^{\gamma 2i} \ldots f_k{}^{\gamma ki}$$

where the γji are the powers for the jth fundamental unit in the ith parameter. Substituting in ωi and making all the exponents equal gives a system of equations that can be expressed in matrix form:

$$\begin{pmatrix} \gamma 11 & \gamma 12 & \cdots & \gamma 1n \\ \gamma 21 & \gamma 22 & \cdots & \gamma 2n \\ \vdots & \vdots & \ddots & \vdots \\ \gamma k1 & \gamma k2 & \cdots & \gamma kn \end{pmatrix} \begin{pmatrix} \alpha 1 \\ \alpha 2 \\ \vdots \\ \alpha n \end{pmatrix} = \begin{pmatrix} \beta 1 \\ \beta 2 \\ \vdots \\ \beta n \end{pmatrix}$$

The matrix γji tells us how to convert between the parameters and the dimensions.

The matrix in a more compact notation:

$$\bar{\bar{\gamma}} \, \bar{\alpha} = \bar{\beta}$$

This equation is very useful, because tells the way to combine the parameters to get the right units, and obtain the parameters of the system involving all the fundamental units.

Supposing nondimensional parameters a particular combination of α's and nondimensional parameter denoted by π.

The equation can be written as

$$\bar{\bar{\gamma}} \, (\overline{\alpha o} + \overline{\pi}) = \bar{\beta}$$

The non dimensional parameter π does not change the units, because is dimensionless, so can be subtracted the following statement

$$\bar{\bar{\gamma}} \, \bar{\pi} = 0$$

The solution is the zero vector, and is called the nullspace of a matrix, in this case of the matrix γ. So this statement says that the π has no dimensions, the nullspace of the system gives the dimensionless parameters.

The rank nullity theorem can be written in a simpler form like

$$\text{Rank}(\bar{\bar{\gamma}}) + \dim\big(nullspace(\bar{\bar{\gamma}})\big) = number \ of \ columns$$

The number of columns is the fundamental units k, and the number of columns the number of parameters n.

Then, the dimensionless parameters are

$$p = n - k$$

Applying this method to our System of equations gives

Parameter	Dimensions
L	Length
R (Gas constant)	$(energy)T^{-1}mol^{-1}$
T (Temperature)	T
F (Faraday's constant)	$(charge)\ mol^{-1}$
C (concentration)	$mol\ (length)^{-3}$
C_o (reference concentration, ej. bulk)	$mol\ (length)^{-3}$
ε (permittivity)	$(charge)^{-2}(energy)^{-1}(length)^{-1}$
D (diffusivity)	$(length)^2(time)^{-1}$
u (velocity)	$(length)(time)^{-1}$
x (axial direction)	length
t (time)	time
ψ (electrical potential)	$charge\ (energy)^{-1}$
ρ_{fix}	$charge(length)^{-3}$

$$
\begin{pmatrix}
 & L & R & T & F & C & C_o & \varepsilon & D & u & x & t & \psi & \rho_{fix} \\
\text{mol} & 0 & -1 & 0 & -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{Length} & 1 & 0 & 0 & 0 & -3 & -3 & -1 & 2 & 1 & 1 & 0 & 0 & -3 \\
\text{T} & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{Charge} & 0 & 0 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 1 & 1 \\
\text{energy} & 0 & 1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 \\
\text{time} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 1 & 0 & 0
\end{pmatrix}
$$

The matrix has Rank=6 and 13 columns, by the nullity theorem the number of dimensionless parameters is

$$\dim\big(nullspace\,(\bar{\bar{\gamma}})\big) = 7$$

Gives the null space matrix

	L	R	T	F	c	C₀	ε	D	u	x	t	ψ	ρ_{fix}
Π_1	0	0	0	1	0	1	0	0	0	0	0	0	-1
Π_2	0	-1	-1	1	0	0	0	0	0	0	0	-1	0
Π_3	2	0	0	0	0	0	0	-1	0	0	-1	0	0
Π_4	1	0	0	0	0	0	0	0	0	-1	0	0	0
Π_5	-1	0	0	0	0	0	0	1	-1	0	0	0	0
Π_6	2	-1	-1	2	0	1	-1	0	0	0	0	0	0
Π_7	0	0	0	0	1	-1	0	0	0	0	0	0	0

The dimensionless parameters are

$\Pi_1 = \dfrac{F\,Co}{\rho_{fix}}$	$\zeta_{fix} = \dfrac{\rho_{fix}}{F\,Co}$	Dimensionless fix charge density
$\Pi_2 = \dfrac{F\,\psi}{R\,T}$	$\Psi = \dfrac{F\,\psi}{R\,T}$	Dimensionless electrical potential
$\Pi_3 = \dfrac{D\,t}{L^2}$	$\tau = \dfrac{D\,t}{L^2}$	Dimensionless time scale
$\Pi_4 = \dfrac{x}{L}$	$\xi = \dfrac{x}{L}$	Dimensionless length scale
$\Pi_5 = \dfrac{D}{L\,u}$	$Pe = \dfrac{u\,L}{D}$	Peclet Number
$\Pi_6 = \dfrac{L^2 F^2\,Co}{\varepsilon\,R\,T}$	$\tilde{\lambda}_D^2 = \dfrac{\varepsilon\,R\,T}{L^2 F^2\,Co}$	Dimensionless Debye length (electrical double layer)
$\Pi_7 = \dfrac{c}{Co}$	$\theta = \dfrac{c}{Co}$	Dimensionless concentration

Can be seen that this method is very powerful, because all the parameters obtained have physical significance, and only with the matrix of the governing parameters can be obtained all the dimensionless parameters that governing the system.

APPENDIX 3: MATHEMATICA CODE

```
Quit[]

"Parameters of the system"

ri = 2 * 10^(-9); rp = 2 × 10^(-9); "m"
D1 = 1.33 * 10^(-9); "m2/s"
D2 = 2 * 10^(-9); "m2/s"
C0 = 0.5; "mol/m3"
L = (200 * 10^(-9)); "m"
epsil = 78.5 * (8.85 * 10^(-12)); "F/m"
F = 96 485; K = 1.38 * 10^(-23); "C/mol"
T = 293; "K"
R = 8.314; "J/mol K"
Dbye = ((epsil R T) / (C0 F^2))^(1/2)

"Hindrance factor of diffusion and velocity"

lamda = ri / rp;
phi = (1 - lamda)^2;
Kic = (2 - phi) (1 + 0.054 lamda - 0.988 lamda^2 + 0.441 lamda^3);
Kid = 1 - 2.3 lamda + 1.154 lamda^2 + 0.224 lamda^3;
```

$$visc = 1000 \left(1 + 18 \frac{2\, ri}{rp} - 9 \left(\frac{2\, ri}{rp}\right)^{\wedge}2\right);$$

```
D1p = Kid (D1) visc;
D2p = Kid (D2) visc;
vv = 0.03;
uu = Kic vv
```

```
"Declare grid and n°points"
npts = 500; order = 5;
nx = Range[0, 1, 1 / (npts - 1)];


"Parameters declared as HeavisideFunctions"
Dii = D1 UnitStep[nx] - (D1 - D1p) UnitStep[nx - 0.25] + (D1 - D1p) UnitStep[nx - 0.75];
Djj = D2 UnitStep[nx] - (D2 - D2p) UnitStep[nx - 0.25] + (D2 - D2p) UnitStep[nx - 0.75];
uv = vv UnitStep[nx] + (uu - vv) UnitStep[nx - 0.33] - (uu - vv) UnitStep[nx - 0.75];
cdens = (2 UnitStep[nx - 0.25] - 2 UnitStep[nx - 0.75]);


"Dimensionless parameters"



Pe1 = (uv L) / Dii;
Pe2 = (uv L) / Djj;
Dbyy = (Dbye / L) ^ 2
"Steric coefficient ( in this case 0)"
σ = 0;

 "Discretization of the derivatives"

 {ddx, d2dx2} =
   Map[
    NDSolve`FiniteDifferenceDerivative[Derivative[#], nx, "DifferenceOrder" → order][
      "DifferentiationMatrix"] &, {1, 2}];
"Sodium"
n = Array[nn[#][t] &, npts];
"Chloride"
c = Array[cc[#][t] &, npts];
"Potential"
v = Array[vf[#][t] &, npts];


"Declare the system of Nernst Planck with steric effects (if the steric
  coefficient = 0 without steric effects) and Poisson equations"

eqn1 = Thread[D[n, t] == d2dx2.n + ddx.(n ddx.v) - Pe1 ddx.n + σ n d2dx2.c + σ n d2dx2.n];
eqn2 = Thread[D[c, t] == d2dx2.c - ddx.(c ddx.v) -  Pe2 ddx.c + σ c d2dx2.n + σ c d2dx2.c];
eqn3 = Thread[-Dbye d2dx2.v == n - c - cdens];


"Boundary condition"

eqn1[[1]] = n[[1]] == 1;
eqn1[[-1]] = ddx[[-1]].n == 0;
eqn2[[1]] = c[[1]] == 1;
eqn2[[-1]] = ddx[[-1]].c == 0;
eqn3[[1]] = v[[1]] == 0;
eqn3[[-1]] = ddx[[-1 ]].v == 0;
```

```
"initial conditions (t=0)"

ic1 = Thread[n == 0] /. t → 0;
ic2 = Thread[p == 0] /. t → 0;
ic3 = Thread[c == 0] /. t → 0;


"Solve the system of DAE's and store the solution"
vars = Flatten[{n, v, c}] /. x__[t] :> x;
PDEsol = First[NDSolve[{eqn1, eqn2, eqn3, ic1, ic2, ic3}, vars, {t, 0, 1}]];
time = Flatten@First[vars[[1]] /. PDEsol];
{nsol, vsol, csol} =
    Flatten[Table[Transpose[{nx, ConstantArray[ti, npts], # /. PDEsol}] /. t → ti,
        {ti, time[[1]], time[[2]], 0.1}], 1] & /@ {n, v, c};


"Example of 3D Plot of the solutions in order ( Sodium, Chloride)"

GraphicsRow[ListPlot3D[#, PlotRange → All, PlotTheme → "Classic", Mesh → {50, 50}] & /@
    {nsol, csol}]
```