The Application of Generalised Maxwell-Stefan Equations to Protein Gels

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Abstract

The removal of milk fouling deposits often requires the diffusion of electrolyte solutions such as sodium hydroxide through a gel. Very often more than one single anion and one single cation are involved and thus the modelling of such diffusion requires a multicomponent description. Diffusion of electrolyte solutions through gels can be modelled using the Maxwell-Stefan equation. The driving forces for diffusion are the chemical potential gradients of ionic species and the diffusion potential, i.e., the electrostatic potential induced by diffusion of the ions. A model based on the Maxwell-Stefan equation was applied to electrolyte solutions and electrolyte solutions with a gel. When modelling the diffusion of electrolyte solutions, the resulting equations were found to be a partial differential algebraic equation system with a differentiation index of two. The identification of this characteristic of the system enabled a solution method using the method of lines to be developed. When modelling the diffusion of electrolyte solutions through a gel an explicit expression for diffusion potential was developed and hence the diffusion equations were solved. Numerical solutions were presented for a number of case studies and comparisons were made with solutions from literature and between different electrolyte systems. It was found that the results of diffusion of electrolytes were in good agreement with those of experiments and literature. In the case of diffusion of electrolytes through a gel, swelling of the gel was predicted. The model can be improved by adding thermodynamic factors and can be easily extended to multiple ion systems.

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Table of contents

Nomenclature

A Cross sectional area of membrane [m^2]

$\left[B^n\right]$ Matrix function of inverted binary diffusion coefficients defined by Equations (2.2.12a) and (2.2.12b) [s/m^2]

c_t Total molar concentration [mol/m^3]

C_i Mo[1]ar concentration of species *i* used in Fick's equation [mol/m^3]

c_H Molar concentration of undissociated protons [mol/m^3]

c_H^* Molar concentration of undissociated protons in equilibrium with a given OH- concentration [mol/m^3]

c_{OH^-} Molar concentration of OH- [mol/m^3]

D Fickian diffusion coefficient [m^2/s]

$\mathcal{D}_{ij}$ Maxwell-Stefan diffusivity between species *i* and *j* [m^2/s]

$D_{i,eff}$ Effective diffusion coefficient of component *i* in multicomponent mixture [m^2/s]

D_0 Diffusion coefficient of the species in free solutions in Equation (2.2.19) [m^2/s]

$\mathcal{D}_{in}^o$ Infinite dilution diffusivity for component *i* present in trace amounts in component *n* [m^2/s]

F_i Net driving force on component *i* in Equation (1.2) [N]

F_i Force acting per mole of species *i* in Equation (2.2.7) [N/mol]

$\tilde{F}_i$ Force acting per unit mass of component *i* [N/kg]

$\Im$ Faraday's constant, 9.65×104 [C/mol]

i Current in Section 2.2.3 [amps]

i Mole fraction analogue of the ionic strength [-]

J_i Molar diffusion flux of component *i* [mol/m^2 s]

$J_{i,k}$ Molar diffusion flux of component *i* from segment k to k+1 [mol/m^2 s]

J_i^n Molar diffusion flux vector of species *i* with respect to species *n* [mol/m^2 s]

M_c Average molecular weight between two junctions in a polymer chain [kg/mol]

N_i Molar flux of component *i* [mol/m^2 s]

N_t Mixture molar flux referred to a stationary coordinate reference frame [mol/m^2 s]

$n_{i,k}$ Number of moles of component *i* in segment k [mol]

n_H Number of undissociated sites per polymer [-]

P System pressure, [Pa]

R Idea gas constant, 8.31414 [J/mol K]

$r_{i,k}$ Rate of generation of component *i* in segment k [mol/m^3 s]

t Time [s]

T Temperature [K]

u Diffusive velocity [m/s]

V Volume of polymer or gel [m^3]

$\bar{V}_i$ Partial molar volume of component *i* [m^3/mol]

$\bar{V}_s$ Partial molar volume of the solvent (water), usually 0.018 [m^3/mol]

V_k Volume of segment k [m^3]

x_i Mole fraction of component *i* [-]

z Distance dimension [m]

z_i Charge number of component *i* [-]

Greek Letters

γ_i Activity coefficient of component *i* in solution [-]

ϕ Diffusion potential [V]

ϕ_0 Polymer volume fraction at initial state in Equation (2.2.15) [-]

ϕ^V Volume fraction of polymer in the gel [-]

ρ_i Density of component i [kg/m^3]

ρ_n Density of the polymer network in dry solid state [kg/m^3]

Φ Network functionality, usually 3 or 4 and here was chosen 4

ζ_{ij} Friction coefficient between component i and j [N s/mol m]

μ_i Chemical potential of component i [J/mol]

Γ Matrix of thermodynamic factors with elements defined by Equation (2.2.13a)

δ_{ij} Kronecker delta, 1 if $i = j$, 0 if $i \neq j$ [-]

χ Flory-Huggins parameter [-]

λ Ratio between the radius of the polymer chain and the diffusion molecule [-]

ν^* Molar density of elastically active network chains [mol/m^3]

Subscripts

s Referring to the solvent

p Referring to the polymer

w Denotes to water

δ Quantity evaluated at membrane surface

0 Referring to the initial state

i, j Component indices

k Segment numbers

n The number of components

Superscripts

o Referring to the pure liquid in Equation (2,2,14) and the infinite dilute solution in Equation (2.2.27)

' Referring to in the membrane

Mathematical Symbols

∇	Gradient
Δ	Difference operator

Matrix Operations and Notation

$( )$	Column matrix
$[ ]$	Square matrix
$[ ]^{-1}$	Inverse of a square matrix

1 Introduction

1.1 Protein gel, milk fouling and drug delivery

Milk is composed of water, carbohydrate, fat, protein, minerals and vitamins. Pasteurisation and sterilisation are generally used in milk processing. In pasteurisation, milk receives mild heat treatment to reduce the number of bacteria present. In sterilisation, milk is subjected to severe heat treatment that ensures almost complete destruction of the microbial population. This results in the fouling deposits on heat transfer equipment surfaces. The deposits consist of proteins, fats, sugars and mineral salt. Among them, whey proteins, and especially β-lactoglobulin (βLg) (Mercadé-Prieto et al., 2006, 2007), constitute the bulk of fouling deposits and thus the fouling deposits are considered to be primarily heat-induced gels.

The frequent removal of fouling deposits is required to meet the strict hygiene standards and to maintain normal production capability. It is also critical to the dairy industry in terms of energy and cost efficiency. Cleaning of surfaces often requires the diffusion of electrolyte solutions such as sodium hydroxide through a gel. Very often more than one single anion and one single cation are present and thus the modelling of such diffusion requires a multicomponent description. In the case of protein deposit, the protein gel is likely to be charged and is thus an extra ionic component. There have been numerous studies of diffusion into polyelectrolyte system. Some early experiments were carried out by Loeb (1921) who used gelatine in the presence of HCl and any one of NaCl, $NaSO_4$, or $CaCl_2$ and found the swelling, electrical potential and osmotic pressure were affected by the ionic concentration. More recently Mercadé-Prieto and co-workers (Mercadé-Prieto et al., 2006, 2007) have considered cases where, in addition to charged βLg protein gel, at least three other ions are involved. However, little attention has been paid to the dynamic diffusion modelling of the alkali ions from the bulk solution into the gel.

Whey proteins are also by-products of the cheese industry. They are widely used in foods primarily for their superior gelling and emulsification properties. Recently,

research on the physicochemical properties of the whey proteins suggests that they may be suitable for many novel applications in food and bioprocess systems. For example, they may be used as pH-sensitive hydrogels for the controlled delivery of biologically active substances and they may be formed into nanoparticales which entrap drugs or bioactive compounds within but not chemically bound to them (Gunasekaran, et al., 2007). Gunasekaran et al. (2007) did experiments to investigate the use of whey proteins as pH-sensitive hydrogels and nanoparticle systems. They used caffeine as a model bioactive, and encapsulated this in a commercial whey protein concentrate. They reported that the hydrogels exhibited a pH-sensitive swelling ability especially at pH above their isoelectric point (the point at which the hydrogels are not electrically charged). They also reported that the release of encapsulated model drug from the hydrogels was slower when the pH was below the isoelectric point than it was at a pH above the isoelectric point. This dynamic behaviour also involves the diffusion of ions into the gel.

1.2 Maxwell-Stefan diffusion and Fickian diffusion

There are two common ways to describe a multicomponent diffusion system. People tend to use Fick's equations:

$$J_i = -D\frac{dC_i}{dz} \tag{1.1}$$

where C_i is the molar concentration of species i [mol/m^3], J_i is the molar flux of components i [mol/m^{2}s], D is the Fickian diffusion coefficient [m^2/s], and z is the distance dimension [m].

Alternatively, the Maxell-Stefan approach describes the system as 'driving force equals friction'. It is described by Wesselingh and Krishna (2000), and can be written in the form

$$F_i = \sum_{j \neq i} \zeta_{ij} x_j \left(u_i - u_j\right) \tag{1.2}$$

where F_i is the net driving force on component i, ζ_{ij} is the friction coefficient between components i and j and u are the diffusive velocities. The driving forces often used are

chemical potential gradient and electrical force. By substituting the driving force and the friction coefficient into equation (1.2), it can be written as

$$-RT\frac{d\ln(\gamma x)_i}{dz}-\overline{V}_i\frac{dP}{dz}-\Im z_i\frac{d\phi}{dz}=\sum_{j\neq i}\frac{RT}{c_t Đ_{ij}x_i}\left(x_j N_i-x_i N_j\right) \qquad (1.3)$$

where x_i - mole fraction of component i

γ_i - activity coefficient of component i in solution

R - idea gas constant, 8.31414 [J/mol K]

T - temperature [K]

P - system pressure, [Pa]

$\overline{V}_i$ - partial molar volume of component i [m^3/mol]

z_i - charge number of component i

$\Im$ - Faraday's constant, 9.65×10^4 [C/mol]

ϕ - electrical potential [V]

c_t - total molar concentration [mol/m^3]

N_i - molar flux of component i [mol/m^2 s]

$Đ_{ij}$ - Maxwell-Stefan diffusivity between species i and j [m^2/s]

dz - distance dimension [m]

Looking at equation (1.1), one can see that the Fickian equation uses the concentration gradient as the major driving force. However, this is questionable. Wesselingh and Krishna (2000) have shown that in a solution of sodium chloride and hydrogen chloride sodium will diffuse against its gradient, in the direction opposite to what we expect from Fick's law. For the problem in this thesis which involves multiple ions, Fickian equation cannot be applied accurately. In addition, Fickian equation becomes less straightforward when there are more than two components in a system.

In contrast, equation (1.3), the Maxwell-Stefan (MS) equation, is much more flexible. It does yield Fick's equation as a limiting case for some simple problems, such as dilute and thermodynamically ideal solutions. It can also take into account effects such as viscous flow, electrostatic potential, pressure, and thermodynamic activity. A thorough

description of advantages of the MS equation over the Fick's equation is given by Krishna and Wesselingh (1997). In this thesis, the MS equation has been used as the theoretical base.

1.3 Aim of this research

So far, many researchers have established diffusion models of system of a gel and electrolyte. When doing research on the existing models in literature articles, I have found that there are two major limitations. The first set of models is based on Fick's equation. As discussed above, with many limitations, Fick's law cannot provide a reliable solution in the case that involves multicomponents and the gel. The second set of methods assumes thermodynamic equilibrium. Thus, the influence of diffusion potential is given by using the Donnan equilibrium relation and is not given dynamically.

Protein gels in an aqueous solution are strongly negatively charged with a charge number between 10 and 20, and this charge can be influenced by the pH of the surrounding solution (Wesselingh and Krishna, 2000). In this thesis, for a starting point to establish a dynamic model by using MS approach, I firstly investigate an idealised system with a neutral gel and three ions without considering the influence of pH and thermodynamics. Then, as the research goes on, I have established a more generalised model that not only involves a negatively charged gel but also takes the pH of the electrolyte solution into account.

The aim of this work was to develop a theoretical framework and hence to specify the experimental data that might be required for a full understanding of the diffusion in the system containing gel and electrolytes. The model was based on the Maxwell-Stefan equations, and therefore takes the diffusive interaction between components into account to determine which components of the model seem more important than the others. The model is easily extended to multiple ion systems.

2 Literature

2.1 Protein gels

Previous work by researchers in the area of milk fouling is largely focused on the experimental studies in order to obtain a good understanding of the cleaning behaviour. A recent review of milk fouling in heat exchangers is given by Bansal and Chen (2006).

Xin and Chen (2004) did an important experimental study on the removal of a protein foulant from metal surfaces. This work is important for two reasons. Firstly, for the first time, a polymer dissolution concept was used to describe the complicated protein deposit cleaning process. The essential steps of the cleaning are: the diffusion of the cleaning agent from the bulk solution to the surface of the deposit, the reaction of the cleaning agent with the deposit, the formation of the swollen gel and finally the diffusion of the disengaged protein from the gel surface into the bulk solution. Secondly, it proposed a simple mathematical model to estimate the cleaning rate and cleaning time for proteinaceous fouling. The good agreement of experimental results and model predictions supported the modelling concepts used. Although the model in the paper cannot be applied in removing large aggregates, the model provides a good foundation for further studies on the cleaning mechanisms of protein-based milk fouling.

Mercadé-Prieto and Chen (2006) tried to analyse each protein cleaning step proposed by Xin and Chen (2004). In their research, they firstly examined the sodium hydroxide solution diffusivity at different pH at 22 ^{o}C. Then, they studied the influence of dissolution pH. Finally, they considered the influence of temperature on the dissolution process. They found that the diffusivity of NaOH in a protein gel was about two thirds of that in water. They also found that at a low dissolution pH, between 12 and 13, the dissolution rate started from a small value and it reached to a constant value after a time. At a high dissolution pH, on the other hand, this rate showed a decreasing trend. The temperature also played a role on dissolution. They found that at high temperatures, the dissolution rate decreased with time, and the remaining gels became more yellowish.

Mercadé-Prieto et al. did considerable work on the study of heat-induced β-lactoglobulin (βLg) gels. During two years between 2006 and 2007, this research group produced five papers on this field.

Mercadé-Prieto, Falconer, Paterson and Wilson (2006a) investigated the influence of the gel structure on the dissolution rate of heat-induced βLg gels. The dissolution rate profile of βLg gels was found to resemble those reported for whey protein concentrate gels (Mercadé-Prieto and Chen, 2006). The dissolution rate profiles observed at high alkaline pH (>13) was smaller and decreased over time, which was similar to the result reported previously for whey protein concentrate gels (Mercadé-Prieto and Chen, 2006). Therefore, they reached the conclusion that βLg can be used successfully as a model of whey protein. They also developed the idea that swelling may be related to the low dissolution observed at high pH. Using the concept of polyelectrolyte screening developed for polyamphotyle polymers, the group found that at high salt concentrations the swelling ratio of βLg gels decreased. The addition of salts greatly reduced the dissolution rate. However, they did not provide accurate swelling rates at high pH owing to the gels undergoing dissolution.

Mercadé-Prieto, Falconer, Paterson and Wilson (2006b) further studied the influence of the gel structure on the dissolution rate of βLg heat-induced gels. The results were similar to the previous findings (Mercadé-Prieto et al., 2006a). They found that the dissolution behaviour was strongly influenced by the condition under which the gel was formed. At low alkaline pH values (<13), the dissolution rate decreased with longer gelation time and higher temperature. In addition, they observed an inverse relationship between the dissolution rate and the amount of covalently cross-linked proteins in the gel.

Mercadé-Prieto, Sahoo, Falconer, Paterson and Wilson (2007a) studied the polyelectrolyte screening effects on the dissolution of whey protein gels at high pH conditions. In this study, they provided strong evidence that the dissolution rate was

affected by the equilibrium-swelling ratio in βLg gels. The swelling ratio was reduced in the presence of salts because of the polyelectrolyte screening effect of the cations. At high dissolution pH (>13.3), the high sodium ion concentration reduced swelling in spite of the high surface charge of the protein. They also observed that the final dissolution rate of gels pre-soaked in 1M sodium hydroxide or sodium chloride was similar, although their pH values were different. This dissolution rate was much lower than that of untreated gels. The reason for this was that the high sodium ion concentration in the soaked gels hindered swelling, inhibiting the disentanglement of the protein clusters regardless of the high pH.

Mercadé-Prieto, Falconer, Paterson and Wilson (2007b) presented a simple model for the swelling of protein gels including the effect of solvent pH and ionic strength. They developed the model from the statement of swelling equilibrium, which meant the difference between the ionic contributions from the chemical potential inside the gel and in solution equalled the sum of the contributions to the chemical potential of the mixing and elastic forces. Because the model was derived from equilibrium, it cannot be applied for the study of the dynamic behaviour of the swelling mechanism. However, the paper provided many useful experimental results. Particularly, Figure 7 in the paper (Mercadé-Prieto et al., 2007b) showed the effect of the molar electrolyte concentration in solution on the equilibrium swelling ratio for sodium chloride electrolyte.

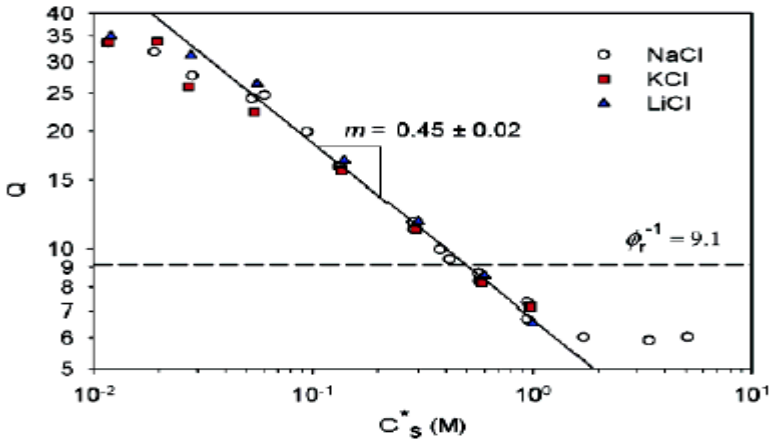


Figure 7. Effect of c_s^* on the equilibrium swelling ratio for NaCl, KCl, and LiCl electrolytes at pH 11.2. The line shows the experimental scaling law found (eq 30). The dashed line shows the *Q* value of the gels in the relaxed state.

Mercadé-Prieto, Paterson and Wilson (2007c) believed that there was a pH below which the dissolution rate was very low and above which the dissolution rate was high. Thus, they carried out a series of experiments to confirm and characterise the existence of such pH threshold for the dissolution of heat-induced βLg gels. They did observe a sharp transition in solubility between pH 11 and 12 and this transition shifted to higher pHs for gels formed at higher temperatures and for longer gelling times. They also found the destruction of large aggregates was faster at higher pH and this destruction also showed a transition between pH 11 and 12.

2.2 Maxwell-Stefan approach

2.2.1 Maxwell-Stefan equations

The Maxwell-Stefan equation has been employed as the theoretical base for the model in this thesis. Thus, it is very important to introduce it before modelling. The Maxwell-Stefan equation was first developed by Maxwell and Stefan around 1870. Later, it was generalised by Taylor and Krishna (1993).

The equation for diffusion of a component *i* is

$$-\nabla_T \mu_i = \sum_j x_j \frac{RT}{Đ_{ij}} \left(u_i - u_j\right) \tag{2.2.1}$$

The term on the left-hand side is the 'driving force' on *i*. It shows that species *i* tends to move down the gradient of its chemical potential. The terms on the right-hand side represent the friction between component *i* and *j*.

The molar flux, N_i, of component *i* can be expressed as

$$N_i = x_i c_t u_i \tag{2.2.2a}$$

where c_t is the total concentration in moles per volume.

The molar flux, N_i, can be related to the molar diffusion flux, J_i, by

$$N_i = J_i + x_i N_t \tag{2.2.2b}$$

By multiplying both sides of equation (2.2.1) by x_i / RT and combining with equation (2.2.2a), the following equation can be obtained:

$$-\frac{x_i}{RT}\nabla_T \mu_i = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_j N_i - x_i N_j}{c_t Đ_{ij}} \tag{2.2.3}$$

Define a quantity d_i:

$$d_i = -\frac{x_i}{RT}\nabla_T \mu_i \tag{2.2.4}$$

It is clear that $c_t RTd_i$ is the force acting per volume of the mixture and that d_i / x_i is the force acting per mole of component *i*.

The Maxwell-Stefan equation can be generalised by including the influence of external force fields. When the system is subject to external body forces like electrostatic potential gradients, it is necessary to redefine the generalised driving force as:

$$c_t RTd_i = -c_i \nabla_T \mu_i + \rho_i \widetilde{F}_i \tag{2.2.5}$$

with $\widetilde{F}_i$ represents the force acting per unit mass of component *i* and ρ_i is the density of component *i*.

The chemical potential gradient term is often expanded to explicitly include the contribution of the pressure gradient.

$$\mu_i = \mu_i^0 + RT\, ln(\gamma x)_i + \overline{V}_i \nabla P \tag{2.2.6}$$

with γ_i the activity coefficients.

If the body force F_i represents the force acting per mole of species *i*, the generalised Maxwell-Stefan (GMS) equation can be written as:

$$d_i = \frac{x_i}{RT}\nabla_T \mu_i + \frac{x_i}{RT}F_i = \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{c_t Đ_{ij}}, i = 1,2,...n \tag{2.2.7}$$

where *n* is the number of species considered.

For isothermal, isobaric transport in electrolyte systems, the body force F_i is the electrical force caused by the electrostatic potential gradient $\nabla\phi$

$$F_i = -z_i \Im \nabla\phi \tag{2.2.8}$$

where z_i is the ionic charge of component *i* and $\Im$ is the Faraday constant.

Thus, the GMS equation in electrolyte systems can be written as

$$\begin{aligned} d_i = \frac{x_i}{RT}\nabla_T \mu_i + x_i z_i \frac{\Im}{RT}\nabla\phi &= \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{c_t Đ_{ij}}, i = 1,2,...n \\ &= \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i J_j^n - x_j J_i^n}{c_t Đ_{ij}}, i = 1,2,...n-1 \end{aligned} \tag{2.2.9}$$

where J_i^n is the molar diffusion flux vector of species *i* with respect to species *n*.

This equation can be applied to only *n*-1 components at it deals with relative diffusional flux. The n^{th} component, usually taken to be water, is solved by a "bootstrap" relationship. This might come from the stoichiometry of a subsequent reaction, from equilibrium or might be as simple as zero flux for the last component:

$$J_n = 0 \tag{2.2.10}$$

The next step is to rearrange these equations into a form which can be solved numerically. By applying standard linear algebra techniques, these equations can be worked into the following *n*-1 dimensional form:

$$\left(\mathrm{J}^n\right) = -c_t \left[\mathrm{B}^n\right]^{-1} \left(\mathrm{d}\right) \tag{2.2.11}$$

where the B_{ij}^n are defined by:

$$B_{ii}^n = \sum_{\substack{j=1 \\ i\neq i}}^{n} \frac{x_j}{Đ_{ij}} \quad i = 1,2,...,n-1 \tag{2.2.12a}$$

$$B_{ij}^n = -\frac{x_i}{Đ_{ij}} \quad i \neq j = 1,2,...,n-1 \tag{2.2.12b}$$

Further, the first term in driving force, d_i, can be written as

$$\frac{x_i}{RT}\nabla_{T,P}\mu_i = \sum_{j=1}^{n-1}\Gamma_{ij}\nabla x_j \qquad (2.2.13)$$

where

$$\Gamma_{ij} = \delta_{ij} + x_i \left.\frac{\partial \ln \gamma_i}{\partial x_j}\right|_{T,P,\Sigma} \qquad (2.2.13a)$$

Here Γ is a matrix of thermodynamic factors accounting for the non-ideality of the system and δ_{ij} equals one only when $i=j$.

This derivation can be found in the classic multicomponent mass transfer textbook (Taylor and Krishna, 1993).

2.2.2 A GMS worked example

Next, it is useful to present a GMS worked example, which was the swelling of Dextran gels (Bisschops, et al., 1998). In this paper, the author aimed to demonstrate the potentials of the generalised Maxwell-Stefan approach for describing the swelling kinetics of hydrogels. Although, this model only had two components which was a little far from multicomponent system, it was still valuable because the volumetric change of the gel particle as well as the intra-particle shrinking-core behavior was included.

This example was a two-component system composed of the solvent (water) and the polymer: G25, a type of Sephadex dextran gel. Choosing the solvent to be the object, the author defined the driving force and the friction force to obtain the GMS relation.

A. Driving force on the solvent

The author defined the net driving force as the chemical potential gradient of solvent. The expression for the chemical potential in the system of the hydrogel and the solvent was made up of three parts.

- the entropic part, representing the mixing of the polymer network and the solvent.
- the enthalpic part, accounting for the interactions between the network and the solvent molecules.

- the elastic force of the network, which represents the work required for the network swelling, leading to a decrease in entropy of the polymer chains.

According to the Flory-Huggins theory, for a binary mixture of polymer and solvent (water), the chemical potential for the solvent is

$$\mu_s - \mu_s^{\,o} = RT\left(\underbrace{ln\left(1-\phi^V\right)+\phi^V}_{\substack{entropic \\ contribution}} + \underbrace{\chi\phi^{V\,2}}_{\substack{enthalpic \\ contribution}} \right) \tag{2.2.14}$$

where: ϕ^V represents the volume fraction of polymer in the gel and χ is the Flory-Huggins parameter, and $\mu_s^{\,o}$ is the chemical potential in the pure liquid.

The driving force of elasticity is described as the derivative of the Helmholtz energy of the hydrogel with respect to the volume. There are two common models: the affine network model and the phantom network model. In this case, Bisschops *et al.* used the latter because he believed that the phantom one performed slightly better at high swelling ratios. The relation of the phantom elasticity is read as

$$\mu^{el} = \overline{V}_s RT\left[\frac{\rho_n}{M_c}\left(1-\frac{2}{\Phi}\right)\left(\frac{\phi^V}{\phi_0}\right)^{1/3} \right] \tag{2.2.15}$$

in which:

$\overline{V}_s$ - the partial molar volume of the solvent (water), usually 0.018 [m^3/mol]

ϕ_0 - the polymer volume fraction at initial state

ρ_n - the density of the polymer network in dry solid state

M_c - the average molecular weight between two junctions in a polymer chain

Φ - the network functionality, usually 3 or 4 and here was chosen 4.

The driving force for the swelling process is the gradient of the sum of equations (2.2.14) and (2.2.15):

$$F_{dr} = -\frac{d}{dz}\left(\mu^{FH} + \mu^{el}\right)$$
$$= -\frac{d}{dz}\left(RT\left(ln\left(1-\phi^V\right)+\phi^V + \chi\phi^{V\,2}\right)+\nu_s RT\left[\frac{\rho_n}{M_c}\left(1-\frac{2}{\Phi}\right)\left(\frac{\phi^V}{\phi_0}\right)^{1/3}\right]\right) \quad (2.2.16)$$

B. Friction between the solvent and polymer

According to the GMS relation, the friction force exerted on a component in the system is related to the velocity of that particular component relative to the velocities of other species in the system. For a binary system, it becomes

$$F_{fr,1} = \zeta_{1,2}x_2\left(u_1-u_2\right) = \left(\frac{RT}{Đ_{1,2}}\right)x_2\left(u_1-u_2\right) \quad (2.2.17)$$

Because polymers are cross-linked macromolecules, the volume fraction of the polymer is used in the gel phase instead of the mole fraction. The expression for friction on the solvent molecules now is

$$F_{fr,s} = \left(\frac{RT}{D_{eff}}\right)\phi^V\left(u_s - u_p\right) \quad (2.2.18)$$

where

D_{eff} - the effective diffusion coefficient

ϕ^V - the volume fraction of polymer in the gel

u - the velocity of species in the mixture with s for solvent and p for polymer

C.The effective diffusion coefficient D_{eff}

Polymer networks have some peculiarities. Firstly, the pathway through the medium is longer than the distance in a straight line, which leads to the increase in friction. Secondly, narrow pores increase the friction due to the smaller solute-to-pore diameter ratio. Thus, the authors included these effects when considering the effective diffusion coefficient.

$$D_{eff} = D_0 f\left(\phi^V\right) \quad (2.2.19)$$

in which

D_0 - the diffusion coefficient of the species in free solutions

$f\left(\phi^V\right)$ - the polymer effect function

In this modelling, the authors chose the Ogston model to describe the effective function

$$f\left(\phi^V\right) = exp\left(-\left(1+\lambda\right)\sqrt{\phi^V}\right) \tag{2.2.20}$$

Combining equation (2.2.19) and (2.2.20)

$$D_{eff} = D_0\, exp\left(-\left(1+\lambda\right)\sqrt{\phi^V}\right) \tag{2.2.21}$$

λ -the ratio between the radius of the polymer chain and the diffusion molecule $\lambda = r_p / r_s$

D. Bootstrap relation

The authors defined the swelling process involving the motion of two species: the polymer network moving outward and the solvent molecules moving inward. However, the GMS relation only has one relative velocity of the two species. The additional relation is required which is well known as the "bootstrap relation". According to the continuity equation, at any distance from the centre of the bead, the volumetric flux of the solvent equals the counter flux of the polymer chains by assuming both components incompressible. Based on the above theory, the authors expressed the mass balance as:

$$u_s\left(1-\phi^V\right) + u_p\phi^V = 0 \tag{2.2.22}$$

Rearranging equation (2.2.22), the authors then have the "bootstrap":

$$u_s - u_p = -\left(\frac{1}{1-\phi^V}\right)u_p \tag{2.2.23}$$

E. Mathematical solution of the GMS equation

The complete GMS equation for the swelling hydro gel is now obtained

$$-\frac{d}{dz}\left(\mu^{FH} + \mu^{el}\right) = \left(\frac{RT}{D_0 f\left(\phi^V\right)}\right)\phi^V\left(u_s - u_p\right) \tag{2.2.24}$$

Substituting equation (2.2.23) into (2.2.24)

$$\frac{d}{dz}\left(\mu^{FH}+\mu^{el}\right)=\left(\frac{RT}{D_0 f\left(\phi^V\right)}\right)\phi^V\left(\frac{1}{1-\phi^V}\right)u_p \qquad (2.2.25)$$

The result is

$$u_p(z)=\left(\frac{\partial z}{\partial t}\right)_z=\frac{D_0}{RT}f\left(\phi^V\right)\left(\frac{1-\phi^V}{\phi^V}\right)\frac{d}{dz}\left(\mu^{FH}+\mu^{el}\right) \qquad (2.2.26)$$

in which z - the diffusion direction coordinate

t - diffusion time

This example is used as a test case and its result is documented in Section 3.1.

2.2.3 Diffusion potential in electrolyte systems

In electrolyte systems, when individual ions are considered as components, the diffusion of one or more of the ions will result in a local electrical potential difference that will drag a counter ion in the same direction (Wesselingh and Krishna, 2000). This electrical potential difference is often referred as diffusion potential (Newman and Thomas-Alyea, 2004). When there is a single pair of ions, such as sodium chloride in water, there is no need to involve the diffusion potential as both ions move together to maintain electro neutrality. However, the diffusion potential becomes important when there are more than one species of either anion or cation in electrolyte systems.

There is very little literature about the diffusion potential in electrolyte systems. Fortunately, Taylor and Krishna (1993) provided a method to calculate the diffusion potential in their text book. Another method was provided by Lee (1996).

To begin with, in dilute electrolyte systems, Taylor and Krishna introduced the Nernst-Planck equation to describe the diffusion as a limiting case for GMS. The Nernst-Planck equation is written as

$$N_i=-Đ_{in}^o\nabla c_i-c_i z_i Đ_{in}^o\frac{\Im}{RT}\nabla\phi+c_i u_n \qquad (2.2.27)$$

The superscript ^{o} indicates the infinite dilution limit.

They hold that each species in the system carries with it a current, and then the current carried by the mixture is

$$i = \Im \sum_{j=1}^{n-1} z_j N_j \tag{2.2.28}$$

where $\Im$ is the Faraday constant, z_j is the ionic charge of component j, N_j is the molar flux of component j.

Combining equation (2.2.27) and (2.2.28), the current can be written as

$$i = -\Im \sum_{j=1}^{n-1} z_j Đ_{jn}^{o} \nabla c_j - \frac{\Im^2}{RT} \nabla \phi \sum_{j=1}^{n-1} c_j z_j^2 Đ_{jn}^{o}$$

By this, the unit of the current is amperes per square meter (A/m^2). Because the solvent, species n, carries no charge, there is only n-1 species in the system.

In order to simplify the equation, Taylor and Krishna then obtained the expression for the current carried by the mixture by defining κ

$$i = -\Im \sum_{j=1}^{n-1} z_j Đ_{jn}^{o} \nabla c_j - \kappa \nabla \phi \tag{2.2.29}$$

with

$$\kappa_j = \frac{\Im^2}{RT} c_j z_j^2 Đ_{jn}^{o} \text{ and } \kappa = \sum_{j=1}^{n-1} \kappa_j = \frac{\Im^2}{RT} \sum_{j=1}^{n-1} c_j z_j^2 Đ_{jn}^{o}$$

Equation (2.2.29) can be rearranged to give the expression for the electrical potential:

$$\nabla \phi = -\frac{i}{\kappa} - \frac{\Im}{\kappa} \sum_{j=1}^{n-1} z_j Đ_{jn}^{o} \nabla c_j$$

For the system with no current (i=0), the diffusion potential is

$$\nabla \phi = -\frac{\Im}{\kappa} \sum_{j=1}^{n-1} z_j Đ_{jn}^{o} \nabla c_j \tag{2.2.30}$$

Combining equation (2.2.30) and equation (2.2.27), the molar flux of species i is written as

$$N_i = -Đ_{in}^{o} \nabla c_i + c_i u_n + \frac{t_i}{z_i} \sum_{j=1}^{n-1} z_j Đ_{jn}^{o} \nabla c_j$$

in which, t_i, the transference number, is defined by $t_i = \frac{\kappa_i}{\kappa}$.

In this analysis the interaction between ions and water only is considered. Ion-ion or ion-matrix interaction is ignored.

Another way to calculate the diffusion potential in electrolyte systems is given by Lee in his doctoral thesis (1996).

The start point of his model was to consider the equilibrium state of the electrolyte in the gel and the bath. Then, he had the electrical potential difference across the gel-bath interface as follow:

$$\Delta\phi_i = \frac{RT}{z_i \Im} \ln\left(\frac{a_i^b}{a_i^g}\right)$$

in which a_i is the activity coefficient of the ions and the superscripts *b* and *g* denote bath and gel respectively. The same electrical potential difference is imposed on all ions.

In the next step, he introduced the concept of bulk electro-neutrality effect. The ions with greater diffusivity will tend to move across the gel/membrane at faster rate then those with lower diffusivity. However, such tendency for charge separation induces local electric field among ions, which is going to retard the faster ions and to accelerate the slower ones. He used chemical capacitance model to describe the potential coupling among ions caused by such effect.

$$\Delta\phi_e = \frac{1}{C_{E,i}} \sum_i q_i \text{ , with } C_{E,i} = \frac{\varepsilon A}{d} \qquad (2.2.31)$$

where, $\Delta\phi_e$ - is the induced electric potential

$C_{E,i}$ - is the electric potential coupling capacitance

ε - the dielectric constant of the electrolyte

A - the cross-sectional area of the gel/membrane [m^2]

d - the typical maximum separation of charges in a volume element, $\approx 10^{-10}$ m

q_i - the charge of the ion [coulomb]

Next, by assuming the condition was at near equilibrium, he modelled the electric potential difference between two regions as the average of the potential of the individual ions as (considering ideal solutions or dilute solutions)

$$\phi_{avg} \cong \frac{1}{n}\sum_{i}^{n}\frac{RT}{z_i \Im}\ln\left(\frac{x_{io}}{\bar{x}_i}\right) \tag{2.2.32}$$

Finally, the electric potential across the medium is the combination of equation (2.2.31) and (2.2.32):

$$\phi \cong \phi_{avg} + \Delta\phi_e \cong \frac{1}{n}\sum_{i}^{n}\frac{RT}{z_i \Im}\ln\left(\frac{x_{io}}{\bar{x}_i}\right) + \frac{1}{C_E}\left(\sum_i q_i + q_m\right)$$

with q_m the fixed charge numbers of the membrane.

His method seemed to lack theoretical rigour and I feel doubtful about equation (2.2.31).

2.2.4 Pressure difference

Till now, the diffusion potential in the GMS equation in the literature has been examined. Taking a look at the GMS equation (1.3) again, the next parameter to consider is the pressure gradient in the system. It is not clear from literature how it should be defined.

Krishna (1987) said "in many cases of practical interest the pressure gradients are negligibly small and this term may therefore be neglected". Wesselingh and Vonk (1995) presented a model of polarization at an ultrafiltration membrane. In their system, they had four components, namely water, a negatively charged membrane, a counter-ion and a co-ion. They obtained the pressure difference from the water equilibrium:

$$P - P' = \frac{RT}{\bar{V}_w}\ln\frac{x_{w\delta}}{x'_w}$$

in which $\bar{V}_w$ -the molar volume of water

$x_{w\delta}$ -the mole fraction of water in the membrane surface

x'_w -the mole fraction of water in the membrane

This pressure difference was the osmotic pressure difference between the fluids on both sides of the membrane. Again, the model did not consider non-steady states and its effects. The aim of this thesis is to establish a dynamic model of electrolyte system

containing gel. Therefore, this pressure model is of little use in this modelling. However, for the initial test models, Krishna's assumption that pressure effects are negligible was followed.

2.2.5 Activity coefficients

One of the most important advantages by using GMS equation is to consider the system as a non-ideal solution. In the system containing electrolytes and gels, it is necessary to define the activity coefficients of all combinations: activity coefficients of ions and solvent. And it is also important to consider the effect of polymer on the activities.

Absolute activities, λ, are defined by

$$\mu_i = RT \ln \lambda_i$$

Often the difference in chemical potential from the pure state is of interest

$$\mu_i - \mu_i^o$$

When it is expressed as differences, we have

$$\mu_i - \mu_i^o = RT \, ln \frac{\lambda_i}{\lambda_i^o}$$

The ratios of λ are often denoted a_i and are referred to as activities.

This can also be written as

$$\mu_i - \mu_i^o = RT \, ln \, \gamma_i x_i \qquad (2.2.33)$$

with γ_i the activity coefficients of components.

Activity coefficients for ions in multicomponent electrolytes

There are different models to calculate the activity coefficients in multicomponent electrolytes, and they include Guggenherm's method, Bromley's method, Meissner's method and Pitzer's method (Zemaitis et al., 1986). Due to a lack of parameters and the low ionic strengths, Guggenheim's method is used only for H_2O-NaCl-KCl, H_2O-NaCl-HCl and H_2O-KCl-HCl solutions. From the worked examples provided by Zemaitis, it can be seen that the activity coefficients calculated by Pitzer's method are in better

agreement with the experimental results compared with the results calculated by other methods.

The Pitzer's equations to calculate the activity coefficients for cation C and anion A in a multicomponent solution at 25 °C are:

$$\ln\gamma_C = z_+^2 f^\gamma + \sum_a m_a\left\{2B_{Ca} + \left(2\sum_c m_c z_c\right)C_{Ca}\right\} + \sum_c m_c\left(2\Theta_{Cc} + \sum_a m_a \Psi_{Cca}\right)$$
$$+ \sum_c\sum_a m_c m_a\left(z_+^2 B'_{ca} + |z_+|C_{Ca}\right) + 0.5\sum_a\sum_{a'} m_a m_{a'}\Psi_{Caa'}$$

$$\ln\gamma_A = z_-^2 f^\gamma + \sum_c m_c\left\{2B_{cA} + \left(2\sum_a m_a z_a\right)C_{cA}\right\} + \sum_a m_a\left(2\Theta_{Aa} + \sum_a m_c \Psi_{Aac}\right)$$
$$+ \sum_c\sum_a m_c m_a\left(z_-^2 B'_{ca} + |z_+|C_{Ca}\right) + 0.5\sum_c\sum_{c'} m_c m_{c'}\Psi_{cc'A}$$

where $$f^\gamma = -A_\phi\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right]$$

A_ϕ - the Debye-Hückel constant for osmotic coefficients on a log *e* basis

equation $$A_\phi = \frac{1}{3}\left(\frac{e}{\sqrt{DKT}}\right)^3\sqrt{\frac{2\pi d_0 N_A}{1000}}$$

$b = 1.2$

$I = 0.5\sum_i z_i^2 m_i$, ionic strength

z_i - ionic charge

m_i - ionic molality

a - subscript denoting anions

c - subscript denoting cations

and

$$B_{ij} = \beta_0 + \frac{2\beta_1}{\alpha_1^2 I}\left\{1. - \left(1. + \alpha_1\sqrt{I}\right)exp\left(-\alpha_1\sqrt{I}\right)\right\} + \frac{2\beta_2}{\alpha_2^2 I}\left\{1. - \left(1. - \alpha_2\sqrt{I}\right)exp\left(-\alpha_2\sqrt{I}\right)\right\}$$

$$B'_{ij} = \frac{2\beta_1}{\alpha_1^2 I^2}\left\{-1. + \left(1. + \alpha_1\sqrt{I} + 0.5\alpha_1^2 I\right)exp\left(-\alpha_1\sqrt{I}\right)\right\} +$$

$$\frac{2\beta_2}{\alpha_2^2 I^2}\left\{-1. + \left(1. + \alpha_2\sqrt{I} + 0.5\alpha_2^2 I\right)exp\left(-\alpha_2\sqrt{I}\right)\right\}$$

$$C_{ij} = \frac{C^\phi}{2\left|z_i z_j\right|^{1/2}}$$

$\alpha_1 = 2.0$ for 1-1,2-1,1-2,3-1,4-1 and 5-1 electrolytes

$\alpha_1 = 1.4$ for 2-2 electrolytes

$\alpha_2 = 0.0$ for 1-1,2-1,1-2,3-1,4-1 and 5-1 electrolytes, therefore the last part of the B and B' equations cancel

$\alpha_2 = 12.0$ for 2-2 electrolytes

β_0 - Pitzer's parameter

β_1 - Pitzer's parameter

β_2 - Pitzer's parameter for 2-2 electrolytes

C^ϕ - Pitzer's parameter

Θ - Pitzer's interaction parameter for like charged ions

Ψ - Pitzer's ternary interaction parameter

The mean molal activity coefficient of electrolyte CA in the multicomponent solution can be calculated by combining the ionic activity coefficients:

$$\gamma_\pm = \left(\gamma_C^{\nu_C} \cdot \gamma_A^{\nu_A}\right)^{1/\nu}$$

or

$$\ln\gamma_\pm = \frac{1}{\nu}\left(\nu_C \log\gamma_C + \nu_A \log\gamma_A\right)$$

Solvent (water) activity coefficient

Pitzer presented two equations for calculating osmotic coefficients. One of these is for single electrolyte solutions and the other is for multicomponent solutions. The equation for a multicomponent solution is:

$$\phi - 1 = \left(\sum_i m_i\right)^2 \left\{ \begin{array}{l} 2If^{\phi} + 2\sum_c \sum_a m_c m_a \left(B_{ca}^{\phi} + \frac{\left(\sum mz\right)}{\sqrt{|z_c z_a|}} C_{ca}^{\phi} \right) + \sum_c \sum_{c'} m_c m_{c'} \left(\Theta_{cc'} + I\Theta'_{cc'} + \sum_a m_a \Psi_{cc'a} \right) \\ + \sum_a \sum_{a'} m_a m_{a'} \left(\Theta_{aa'} + I\Theta'_{aa'} + \sum_c m_c \Psi_{caa'} \right) \end{array} \right\}$$

where:
$$f^{\phi} = -A_{\phi} \frac{\sqrt{I}}{1 + 1.2\sqrt{I}}$$

A_{ϕ} - the Debye-Hückel constant for osmotic coefficients on a log e basis equation

I - ionic strength

$B_{ca}^{\phi} = \beta_0 + \beta_1 \exp\left(-\alpha_1 \sqrt{I}\right) + \beta_2 \exp\left(-\alpha_2 \sqrt{I}\right)$

$\alpha_1 = 1.4$ for 2-2 electrolytes

$\alpha_1 = 2.0$ for others

$\alpha_2 = 12$ for 2-2 electrolytes

$\alpha_2 = 0.0$ for others

m_i - ionic molality

a - subscript denoting anions

c - subscript denoting cations

β - Pitzer's parameter

C^{ϕ} - Pitzer's parameter

Θ - Pitzer's interaction parameter for like charged ions

Ψ - Pitzer's ternary interaction parameter

$\left(\sum mz\right) = \sum_a m_a |z_a| = \sum_c m_c z_c$

The summations are over all cations and anions in the solution. The Θ' term can be neglected for solutions of electrolytes of similar or not too different charges. All the Pitzer's parameters used in calculation can be found in Zemaitis et al. (1986).

Until now, I have discussed the activity coefficients in polymer free electrolytes. For the solvent (water) activity, the polymer effect has not been taken into account. Although

there are a number of limitations on the availability of this relationship, Wesselingh and Krishna (2000) gave the Flory-Huggins (FH) thermodynamics model.

The FH provides a formula at dealing with molecules that are similar chemically, but different greatly in length. It is based on the idea that the chain elements arrange themselves randomly on a three dimensional lattice. The lengthy and complex explanation of the theory will not be given here. The resulting equations of the chemical potential of the solvent in a solvent-polymer mixture are written as:

$$\mu_s - \mu_s^o = RT\left(ln\,\phi_s^V + \phi_p^V + \chi\left(\phi_p^V\right)^2\right)$$

where ϕ^V is the volume fraction, and the subscription s and p denote solvent and polymer respectively, and χ is the Flory-Huggins non-ideality parameter.

The resulting activity of the solvent with a polymer is (Wesselingh and Krishna, 2000):

$$a_s = \phi_s^V\, exp\left[\left(1 - \frac{\overline{V}_s}{\overline{V}_p}\right)\phi_p^V + \chi\left(\phi_p^V\right)^2\right]$$

with $\overline{V}$ the molar volume [m^3mol^{-1}]

Wesselingh and Krishna (2000) also pointed out that this equation can be extended to three or more polymeric species as long as there are more χ parameters, one for each pair of species. Further, they discussed the values of χ as follows:

- If χ>0, it means that solvent and polymer are dislike each other
- If χ=0, it means that solvent and polymer are similar
- If χ<0, it means solvent and polymer attract each other

Although the model of activities of electrolytes and solvent/polymer can be found in literature, it is very difficult to use it in real simulation. Firstly, it is not clear how ionic and polymer effects should be combined to the solvent activity. Secondly, many parameters, like χ, are simply not available. The influence of the charge number of the gel on the activity of ions and solvent is not known. Finally, there are very few validations of the accuracy of such relationships. Therefore, in this work, solutions are

assumed to be ideal so that behaviour could be observed with a minimum amount of uncertain data.

2.3 Donnan equilibrium

In a system containing electrolytes and a gel, it is important to know more about the Donnan equilibrium. Donnan equilibrium is established when a membrane separates two solutions of electrolytes one of which has one ion for which the membrane is impermeable, while all the other ions can diffuse through the membrane (Loeb, 1921).

2.3.1 Donnan equilibrium theory

Cussler (1984) pointed out the effects of proteins and other polyelectrolytes (polymer with electrolyte solutions), either when these are in solution on one side of the membrane or when these are components of the membrane itself. At equilibrium, equal concentrations of any small electrolytes will not exist throughout these systems. For example, if a membrane containing fixed anionic charges is placed in a sodium chloride solution, the sodium chloride concentration in the membrane will be different than if the membrane had no charge, even if all solutions are behaving ideally.

Cussler (1984) gave the mathematical description considering a simple case: electrolyte diffusion across an uncharged membrane. For the cation 1, the definition of equilibrium across the interface is

$$\mu_1 = \mu_1'$$

$$\mu_1^o + RT\,ln\,C_1 + z_1 \Im \phi = \left(\mu_1^o\right)' + RT\,ln\,c_1 + z_1 \Im \phi' \qquad (2.3.1a)$$

where the primed and unprimed variables refer to the membrane and to the adjacent solution, respectively. C is the concentration at boundary and c is the concentration in the membrane. The Cussler's description assumes that solutions are ideal. A similar equality exists for the anion 2:

$$\mu_2^o + RT\,ln\,C_2 + z_2 \Im \phi = \left(\mu_2^o\right)' + RT\,ln\,c_2 + z_2 \Im \phi' \qquad (2.3.1b)$$

Cussler (1984) said that equation (2.3.1a) and (2.3.1b) described the new "Donnan equilibria", which were the natural result of chemical potentials. However, in this description, the pressure term in chemical potential equations did not appear.

Wesselingh and Vonk (1995) presented another description of Donnan equilibrium. They considered a solution consisting of four components: 1-water, 2-a negatively charged polyelectrolyte such as a protein, 3-a counter-ion such as Na^+, and 4-a co-ion such as Cl^-. The solution was ideal and forced through an ultrafiltration membrane. In their model, they stated that the composition of the solution next to the membrane was different from that in the bulk. They denoted the mole fractions of the components at membrane surface as $x_{1\delta}$, $x_{1\delta}$, $x_{1\delta}$ and $x_{1\delta}$. This solution was in equilibrium with the solution in the membrane pores, with another composition denotations: x_1', x_2', x_3' and x_4'. Obviously:

$$x_2' = 0 \text{ and } x_3' = x'_4 \tag{2.3.2}$$

The chemical potentials of the three species which are involved in the equilibrium consist of contributions due to the component activities, the electrical potential and the pressure:

$$\mu_{1\delta} = RT\, ln\, x_{1\delta} + \overline{V}_1 P \tag{2.3.3a}$$

$$\mu_1' = RT\, ln\, x_1' + \overline{V}_1 P' \tag{2.3.3b}$$

$$\mu_{3\delta} = RT\, ln\, x_{3\delta} + z_3 \Im \phi + \overline{V}_3 P \tag{2.3.4a}$$

$$\mu_3' = RT\ ln\ x_3' + z_3 \Im \phi' + \overline{V}_3 P' \tag{2.3.4b}$$

$$\mu_{4\delta} = RT\, ln\, x_{4\delta} + z_4 \Im \phi + \overline{V}_4 P \tag{2.3.5a}$$

$$\mu_4' = RT\, ln\, x_4' + z_4 \Im \phi' + \overline{V}_4 P' \tag{2.3.5b}$$

The equilibrium relations for the two ions then became:

$$\mu_{3\delta} = \mu_3' \rightarrow RT\, ln\, x_{3\delta} + z_3 \Im \phi + \overline{V}_3 P = RT\, ln\, x_3' + z_3 \Im \phi' + \overline{V}_3 P' \tag{2.3.6}$$

$$\mu_{4\delta} = \mu_4' \rightarrow RT\, ln\, x_{4\delta} + z_4 \Im \phi + \overline{V}_4 P = RT\, ln\, x_4' + z_4 \Im \phi' + \overline{V}_4 P' \tag{2.3.7}$$

Adding these two equations yielded the Donnan equilibrium relation:

$$RT\left(ln\, x_{3\delta} + ln\, x_{4\delta}\right) + \left(\overline{V}_3 + \overline{V}_4\right)P = RT\left(ln\, x_3' + ln\, x_4'\right) + \left(\overline{V}_3 + \overline{V}_4\right)P' \tag{2.3.8}$$

If the pressure terms were neglected because they were small compared with the others, then the equation became:

$$x_{3\delta}x_{4\delta} = x'_3x'_4$$

The electrical potential difference was obtained by subtracting the equation (2.3.6) and (2.3.7) of the two ions without pressure terms:

$$RT\,ln\,x_{3\delta} - RT\,ln\,x_{4\delta} + 2\Im\phi = 2\Im\phi' \rightarrow \phi - \phi' = \frac{RT}{2\Im}ln\frac{x_{4\delta}}{x_{3\delta}}$$

The pressure difference in the equilibrium was obtained from the water equilibrium relation:

$$\mu_{1\delta} = \mu'_1 \rightarrow RT\,ln\,x_{1\delta} + \overline{V}_1P = RT\,ln\,x'_1 + \overline{V}_1P'$$

Thus:

$$P - P' = \frac{RT}{\overline{V}_1}ln\frac{x'_1}{x_{1\delta}}$$

Bellara and Cui (1998) gave a similar description of Donnan equilibrium.

From the discussion above, it is clear that the Donnan equilibrium is a true equilibrium characterised by a potential difference, an osmotic pressure, and electrolyte difference on both sides of the membrane.

2.3.2 Donnan equilibrium experiments

Experimental studies of the Donnan equilibrium can yield much valuable information. A large number of experimental results relating to the swelling of gelatin under various conditions have been collected. Among them, a serial of experiments done by Loeb (1921) are remarked as the classical ones. Next, I will introduce some of them.

Firstly, they were the experiments of the influence of neutral salts on the potential difference between gelatin chloride solutions and outside solutions. In these experiments, Loeb developed a device that could measure the potential difference between the solution inside the membrane and outside the membrane. Simply, he filled a serial of collodion bags (as a membrane) with different gelatin solutions. These gelatin

solutions were made up of 1 g of isoelectric gelatin dissolved in solutions of NaCl with molar concentrations from 1/4,096 M to 1 M. To every solution enough HCl was added that the pH of the solution was 3.5. Then, these bags were dipped into beakers containing the mixture of 350 cm^3 of HCl solution of pH 3.0 and NaCl solutions of different concentrations. At the beginning of the experiments, the concentration of the NaCl in the beaker was always identical with that in the gelatin solution inside the collodion bag. The final measurements were made with the aid of a Compton electrometer after 18 hours when the osmotic and the membrane equilibrium were established. Loeb found that the influence of the hydrogen ion concentration on the potential difference of a gelatin chloride solution was similar to that of the hydrogen ion concentration on the osmotic pressure, swelling, and viscosity of gelatin solutions. He also found that the potential difference calculated by multiplying the values of potential of hydrogen inside minus that outside by 59 agreed quite closely with the observed potential difference.

Secondly, I will introduce the experiments of hydrogen ion and chlorine ion potentials. In these experiments, inside the collodion bag was a 1% solution of gelatin chloride of different pH, outside water. After 18 hours equilibrium was established between inside and outside solutions. The potential of chlorine ion was determined in two different ways. Both led to the result that the values of potential of chlorine ion outside minus potential of chlorine ion inside were, for the same solution, equal to the values of potential of hydrogen inside minus potential of hydrogen outside. Therefore, the same theoretical potential difference could be obtained regardless of the fact whether the value was calculated on the basis of the difference of hydrogen potential inside minus outside or potential of chlorine ion outside minus inside.

Finally, Loeb concluded that since the Donnan equilibrium determined the potential difference, the similarity between the variation of potential difference and that of the osmotic pressure and swelling raised the question whether or not the osmotic pressure and swelling were also determined by the Donnan equilibrium.

Later Loeb, Northrop and Kunitz (1926) carried out a number of osmotic pressure experiments trying to answer the question raised by Loeb. It was found that in every case a considerable increase in swelling was obtained accompanied by a proportional change in osmotic pressure. Therefore, the similarity between osmotic pressure and swelling did exist in the case of salts, acid or alkali. It was also found that a non-diffusible ion (protein) was formed with one of the salt ions and that a Donnan equilibrium was established. However, the osmotic pressure calculated from the Donnan equilibrium was found to be much smaller than that observed, except in the case of aluminium chloride, where the calculated and observed pressures agreed quite well.

2.4 Analytical solution

In order to solve a real multicomponent diffusion system, it is necessary to solve the GMS equations and a mass balance equation:

$$-RT\frac{d\,ln(\gamma x)_i}{dz}-\bar{V}_i\frac{dP}{dz}-\Im z_i\frac{d\phi}{dz}=\sum_{j\neq i}\frac{RT}{c_t Đ_{ij}x_i}\left(x_j N_i-x_i N_j\right) \qquad (2.4.1)$$

in which, *i* refers to the diffusion component.

The continuity equations are:

$$\frac{\partial c_i}{\partial t}=-\nabla\cdot N_i \qquad (2.4.2)$$

Before the development of the computer technology, it is very difficult to solve the equations above as the differential equations governing the process are coupled. It has led many researchers to use simpler constitutive relations that avoid the mathematical complexities. One method was developed in the early 1960s, called the linearised theory, by Toor and by Stewart and Prober. The other one was given by Bird et al.. Taylor and Krishna (1993) explained both methods in their textbook in detail.

2.4.1 The linearised theory

To begin with, it is always convenient to write GMS equations in matrix form, and it is convenient to write the continuity equations in matrix as well. If the solution is ideal

and the driving force does not include pressure and potential effects, the GMS equation (2.2.11) has the simple form:

$$(\mathbf{J}) = -c_t[\mathbf{B}](\nabla \mathbf{x}) \tag{2.4.3}$$

and

$$\frac{\partial(\mathbf{c})}{\partial \mathbf{t}} = -\nabla \cdot (\mathbf{N}) = -\nabla \cdot (\mathbf{J}) - \nabla \cdot (N_t(\mathbf{x})) \tag{2.4.4}$$

Combining those two, the equation is:

$$\frac{\partial(\mathbf{c})}{\partial \mathbf{t}} + \nabla \cdot (N_t(\mathbf{x})) = \nabla \cdot (c_t[\mathbf{B}](\nabla \mathbf{x})) \tag{2.4.5}$$

Equations (2.4.5) represent a set of *n*-1 coupled partial differential equations. Since the matrix **B** is a function of composition it is not always possible to obtain exact solutions without recourse to numerical techniques. The basis of the linearised method is to assume that c_t and **B** can be considered constant. With this assumption, the equations reduce to

$$c_t \frac{\partial(\mathbf{x})}{\partial \mathbf{t}} + \nabla \cdot (N_t(\mathbf{x})) = c_t[\mathbf{B}](\nabla^2 \mathbf{x})$$

or

$$\frac{\partial(\mathbf{x})}{\partial \mathbf{t}} + \nabla \cdot (u(\mathbf{x})) = [\mathbf{B}](\nabla^2 \mathbf{x}) \tag{2.4.6}$$

By doing this, equation (2.4.5) is decoupled to give equation (2.4.6).

To solve the decoupled equations, matrix techniques are needed. Here, I am not going to give the lengthy equation derivation. The details can be found in most classic mass transfer text books (Taylor and Krishna, 1993).

2.4.2 The effective diffusivity methods

Firstly, it is necessary to define the effective diffusivity in terms of the rate of diffusion of component *i* as

$$J_i = -c_t D_{i,eff} \nabla x_i \quad i=1, 2 \ldots n \tag{2.4.7}$$

in which $D_{i,eff}$ is the effective diffusivity of component *i* in the mixture.

The effective diffusivity can also be defined with respect to the molar flux N_i as:

$$N_i = -c_t D_{i,eff} \nabla x_i \quad i=1, 2 \ldots n \tag{2.4.8}$$

Many researchers gave the expression of the effective diffusivity. If the mole fraction gradient is given by equation (2.4.7) and J_i is substituted by the equation (2.2.2b), the mole fraction can be written as

$$\nabla x_i = -\frac{J_i}{c_t D_{i,eff}} = -\frac{\left(N_i - x_i N_t\right)}{c_t D_{i,eff}} \tag{2.4.9}$$

Equation (2.4.9) may be equated to the mole fraction gradient given by the Maxwell-Stefan equation (2.2.7). This produces the Bird equation for the effective diffusivity (Taylor and Krishna, 1993):

$$D_{i,eff} = \left[\left(N_i - N_t x_i\right) \Big/ \left(N_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{\mathcal{D}_{ij}} - x_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_j}{\mathcal{D}_{ij}} \right) \right] \tag{2.4.10}$$

Alternatively, Kubota et al. (1969) gave the expression for $D_{i,eff}$ by fitting the Maxwell-Stefan equation (2.2.7) into the form of equation (2.4.8), and it can be expressed as:

$$\frac{1}{D_{i,eff}} = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{\mathcal{D}_{ij}} \left(1 - \frac{x_i N_j}{x_j N_i}\right) \tag{2.4.11}$$

Use of equation (2.4.7) for the diffusion flux with equation (2.4.2) leads to

$$c_t \frac{\partial x_i}{\partial t} + \nabla \cdot \left(N_t x_i\right) = \nabla \cdot \left(c_t D_{i,eff} \nabla x_i\right)$$

If it is assumed that $c_t D_{i,eff}$ is constant, the above equation simplifies to

$$c_t \frac{\partial x_i}{\partial t} + \nabla \cdot \left(N_t x_i\right) = c_t D_{i,eff} \nabla^2 x_i$$

or

$$\frac{\partial x_i}{\partial t} + \nabla \cdot \left(u x_i\right) = D_{i,eff} \nabla^2 x_i$$

This set of equations can also be solved by applying the same matrix techniques as used in the linearised theory.

Those two analytical methods are practical when fast computers and computing programming techniques are not available. Recently, with the development of computer technology, a problem with mathematic difficulties can be easily solved using some programming packages, such as MATLAB and MathCad. Thus, in this thesis, the built-in solver ODE15s in MATLAB was used to solve the equations.

3 Applications of generalised Maxwell-Stefan equations

3.1 Introduction

The first step in modelling processes is to define a suitable model that can reflect the real situation in a concise and accurate way. In a system containing polymers, such as protein, one needs to be very careful about the chances for over-complicating a model and hence the start point of the modelling is from the simple one.

In the first part of the modelling, I am going to consider diffusion problems in electrolyte systems. To begin with, a simple case is considered: a reservoir of hydrogen chloride solution is connected to another by a very porous gel that causes all the flow to be diffusional but which otherwise does not retard the diffusion. The schematic picture is shown in figure 3.1.1.

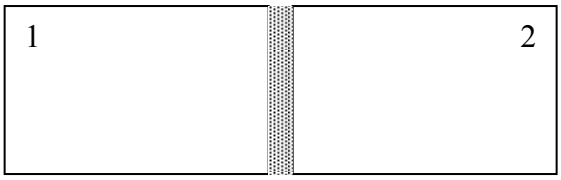


Figure 3.1.1 Schematic of hydrogen chloride diffusion in a reservoir

Initially, both tanks and the gel contain the same dilute solution of HCl. Then, the solution in the right hand side is replaced at a finite speed with water. The model can be extended further by considering the same system with a low concentration of sodium chloride. This time, there are three ions in the solution, namely hydrogen cation, chloride anion and sodium cation. In a third model a sodium chloride and sodium hydroxide mixture is used since sodium hydroxide is often used to remove the milk deposit.

The second part describes the complete model: a multi-electrolyte solution with a negatively charged heat-induced protein gel. The solution is still the sodium chloride and sodium hydroxide mixture.

All these models are based on ideal solutions at 25 °C.

3.2 Diffusion in electrolytes

The generalised Maxwell-Stefan equation for an electrolyte solution, described by Taylor and Krishna (1993), has already been introduced in Section 2.2.1. It is repeated here:

$$d_i = \frac{x_i}{RT}\nabla_{T,P}\mu_i + \frac{x_i\overline{V}_i}{RT}\nabla P + x_i z_i \frac{\mathfrak{I}}{RT}\nabla\phi = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i J_j^n - x_j J_i^n}{c_t Đ_{ij}} \qquad (3.2.1)$$

Here x_i is mole fraction of component i, R is the gas constant, T is temperature, μ_i is chemical potential, $\overline{V}_i$ is partial molar volume, P is pressure, z_i is the charge of component i, $\mathfrak{F}$ is the Faraday number, ϕ is the electrical potential, c_t is the total molar concentration of all components, J is molar diffusion flux, and $Đ_{ij}$ is the Maxwell-Stefan diffusion coefficient for components i and j. The matrix form is

$$\left(\mathbf{J}^n\right) = -c_t\left[\mathbf{B}^n\right]^{-1}\left(\mathbf{d}\right) \qquad (3.2.2a)$$

where the B_{ij}^n are defined by:

$$B_{ii}^n = \sum_{\substack{j=1\\ i\neq i}}^{n} \frac{x_j}{Đ_{ij}} \quad i = 1,2,...,n-1 \qquad (3.2.2b)$$

$$B_{ij}^n = -\frac{x_i}{Đ_{ij}} \quad i \neq j = 1,2,...,n-1 \qquad (3.2.2c)$$

3.2.1 Diffusivities

In order to solve the Maxwell-Stefan equations, the values for the Maxwell-Stefan diffusivities between component pairs, namely anion, cation, water and gel, are needed. The first major problem here is simply that there is no tabulated data available for the diffusivities between polymer and either ions or water. Additionally, there is no data for the diffusivities between likely charged ions. Fortunately, Wesselingh et al. (1995) provides sufficient information to make it possible to estimate order of magnitude of these values.

For a gel free solution, the diffusion coefficients of plus/plus and minus/minus ion pair are negative, with the order of magnitude between 10^{-10} and 10^{-13} m^2s^{-1}. For a solution containing a negatively charged gel, if the gel is considered as a solid matrix, the diffusion coefficients of water/gel, cation/water, anion/water and anion/gel are the values in free solution with a tortuosity correction, between 10^{-9} and 10^{-10} m^2s^{-1}. The diffusivity of cations/gel depends on several things, such as swelling, polymer morphology, ion size, etc. For ions with a single charge, the diffusivity is about 10^{-12} m^2s^{-1}. For ions with a double and triple charge, it is somewhere between 10^{-13} and 10^{-14} m^2s^{-1}.

The diffusion coefficients are obtained from Wesselingh and co-workers and they are shown in Table 3.1.1. In some cases typical values are selected from graphs.

Table 3.1.1 Diffusion coefficients used

Coefficient	Value	Ref
$Đ_{H+,water}$	$9.3x10^{-9}$	Wesselingh and Krishna (2000)
$Đ_{Na+,water}$	$1.3x10^{-9}$	Wesselingh and Krishna (2000)
$Đ_{Na+,protein}$	$5x10^{-11}$	Wesselingh et al. (1995)
$Đ_{OH-,water}$	$5.3x10^{-9}$	Wesselingh and Krishna (2000)
$Đ_{OH-,protein}$	$5.3x10^{-10}$	Kraaijeveld et al. (1995)
$Đ_{Cl-,water}$	$2x10^{-9}$	Wesselingh and Krishna (2000)
$Đ_{Cl-,protein}$	$2x10^{-10}$	Kraaijeveld et al. (1995)
$Đ_{water,protein}$	$1.8x10^{-9}$	Wesselingh et al. (1995)

When only one electrolyte is involved in diffusion, the diffusion coefficient of ion-ion can be calculated by the equation (3.2.3a) (Wesselingh and Krishna, 2000):

$$Đ_{+,-} = 2\left(\frac{1}{Đ_{+,w}} + \frac{1}{Đ_{-,w}}\right)^{-1} \qquad (3.2.3a)$$

When there is more than one electrolyte, Wesselingh and Krishna (2000) also presented an empirical equation for ion-ion diffusion coefficients relating them to ion-water diffusion coefficients

$$Đ_{+,-} = \frac{Đ_{+,w} + Đ_{-,w}}{2} \frac{i^{0.55}}{\left|z_+ z_-\right|^{2.3}} \qquad (3.2.3b)$$

where

$$i = 0.5 \sum_i z_i^2 x_i$$

The same equation applied for $Đ_{-,-}$, but with a negative sign.

Generally, the accuracy of the model will be limited by the accuracy of these values due to such estimation.

3.2.2 GMS PDAE system description

In order to obtain the numerical solution of our model of GMS equations, it is necessary to carefully analyse the model equations in the first place.

Equation (3.2.2) can be applied to only *n*-1 components at it deals with relative diffusion flux. The last component is using solved by a "bootstrap" relationship. This might arise from the stoichiometry of a subsequent reaction, from equilibrium or might be as simple as zero flux for one component, e.g.

$$J_n = 0 \qquad (3.2.4)$$

To solve a real system a mass balance equation might also be required. Consider a one dimensional diffusion problem. Here it might be written for a finite segment *k*

$$\frac{dn_{i,k}}{dt} = \left(J_{i,in} - J_{i,out}\right)A \qquad (3.2.5)$$

where $n_{i,k}$ is the number of moles in a small segment, A is the diffusion section area. For the diffusion length dz, if the total molar concentration is constant, it can also be written as:

$$Ac_t dz \frac{dx_{i,k}}{dt} = \left(J_{i,in} - J_{i,out}\right)A \qquad (3.2.6)$$

or

$$\frac{\partial x_i}{\partial t} = \frac{1}{c_t} \frac{\partial J_i}{\partial z} \quad i = 1, n \qquad (3.2.7)$$

In this work, equation (3.2.5) will be used.

In the case with given pressure and electrical potential the system of equations consists of equation (3.2.2) (n-1 equations), a bootstrap relationship, e.g. (3.2.4) and equation (3.2.5) (n equations). The variables of the system are x_i and J_i of which there are n of each.

A solution method such as the method of lines (Schiesser, 1991) is easily applied to such as system.

3.2.3 An index 2 differentiation problem

Now, the same system is considered but involving the diffusion of ions in water through a stationary polymer without any applied electrical potential.

As described by Wesselingh and Krishna (2000, p123), the diffusion of one ion will result in a local electrical potential difference that will drag a counter ion in the same direction. When there is a single pair of ions, such as NaCl in water, there is no need to involve the electrical potential as the ions can be treated as one component. However, when there is more than one of either anion or cation, the diffusion potential is important. It is reasonable to assume that initially the system was electrically neutral everywhere and to retain this there must be no net current. Thus, an addition condition writes as:

$$\sum_i z_i J_i = 0 \tag{3.2.8}$$

The initial condition is

$$\sum_i z_i x_i = 0 \tag{3.2.9}$$

It is possible that the diffusion could lead to a change in the volume in gel or polymer and one would expect that pressure could be described by an equation relating the strain and a structural modulus of the polymer to pressure within it.

$$P = f\left(\frac{V}{V_0}\right) \tag{3.2.10}$$

Now the system consists of GMS equation (3.2.2) (n-1 equations), a bootstrap relationship, e.g. (3.2.4), equation (3.2.5) (n equations), equation (3.2.8) and equation (3.2.10). The total number of equations is $2n$+2. The variables of the system are x_i and J_i of which there are n of each and also ϕ and P with the total number of $2n$+2. In the initial models, pressure was not included.

Wesselingh and Krishna (2000, p125-6) have given an example of a single pair of ions, the hydrogen ion and chloride ion, for which the equations can be easily manipulated to obtain an explicit solution for the electric potential gradient.

However, in general cases like multi-ion systems, such manipulation is not easily possible and then ϕ is not explicitly defined. When the method of lines is applied the system might be described by a series of small segments, and hence equation (3.2.5) would apply directly. The gradients with respect to z in equation (3.2.2) would be approximated by finite difference approximations. These would implicitly give ϕ. Using the approach given by Martinson and Barton (2000), the resulting system of differential algebraic equations (DAEs) would have a differentiation index of 2. This indicates potential problems in the initialisation and solution of such systems. Many software packages like MATLAB (ODE15S) can only solve DAE systems with index less than 2. Fortunately, Dr. Ken Morison modified the ode15s function by externally specifying consistent initial conditions and by not testing the error of algebraic variables. With this modification, the numerical solution of the model could be obtained with implicit diffusion potential ϕ.

The determination of consistent initial conditions was discussed by Pantelides (1988) and Martinson and Barton (2000) but the method described is not trivial. For some systems a DAE solver will produce consistent initial conditions on the first step if the given values are not far from the correct values. If necessary, initial conditions can be set by starting the system at a well defined condition before ramping the external conditions to the state of interest. This was not found to be necessary.

3.2.4 Diffusion of HCl as a single molecule

Simulation begins by modelling diffusion of hydrochloric acid as a single molecule. According to Krishna (2000), in the system contains only one single electrolyte, although the ions may have different diffusivities, which may cause diffusion potential gradient, the electrolyte still diffuses in water as a single substance. Thus, in this case, the model uses two approaches to compare the results: hydrochloric acid as one component, and alternatively, hydrochloric acid as hydrogen ion and chloride ion separately. Both should have the same result.

Firstly, HCl is treated as one component.

System model

This system consists of two components: hydrochloric acid (component 1) and water (2). Water is chosen to be the reference component. It is assumed that the water had no net diffusion flux so no swelling occurred.

The MS equation

Since water is the reference frame and diffusion is only one dimension *z*, the resulting MS equation for hydrochloric acid in matrix form is:

$$J_1 = -c_t B^{-1} \nabla x_1 = -c_t Đ_{12} \frac{dx_1}{dz} \qquad (3.2.11)$$

where $Đ_{12}$ is the diffusion coefficient of component 1 and 2 pair.

Transport equation

Consider a general mass balance over segment *k* on some component *i*, assuming one dimensional mass transfer. The mass balance equation can be expressed in words as

Accumulation=Input - Output + Generation – Consumption

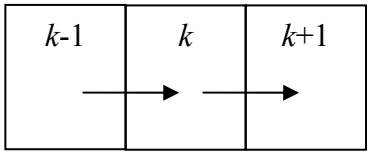


Figure.3.2.1 Diffusion flux into and out segments

In the case there is no chemical reaction in the system, the generation and consumption terms drop out and it is left with

$$\text{Accumulation=Input - Output}$$

For the input into segment k it becomes

$$Input = AJ$$

where A is the cross sectional area [m^2] and J is the diffusion molar flux into the segment k [mol/m^2s]. This flux will be defined as J_{k-1} and similarly for other segments.

A similar expression can also be written for the output from segment k, i.e.,

$$Output = AJ_k$$

Obviously, the accumulation is given by the term involving the derivative of the number of moles in k with respect to time.

$$Accumulation = \frac{dn}{dt}$$

Therefore, the mass balance equations of the component i in segment k, for one dimensional diffusion system, are:

$$\frac{dn_{i,k}}{dt} = \left(J^n_{i,k-1} - J^n_{i,k}\right)A \quad i=1, n \tag{3.2.12}$$

The relationship of the number of moles and mol fraction is given by

$$n_i = c_t x_i A \Delta z \tag{3.2.13}$$

where c_t is the total concentration and Δz is distance between two adjacent segments. Then, equation (3.2.12) can be written as:

$$\frac{d\left(c_t x_i\right)_k}{dt} = \frac{\left(J^n_{i,k-1} - J^n_{i,k}\right)}{\Delta z}$$

If Δz tends towards to zero

$$\frac{d\left(c_t x_i\right)_k}{dt} = \lim_{\Delta z \to 0} \frac{\left(J^n_{i,k-1} - J^n_{i,k}\right)}{\Delta z}$$

Thus:

$$\frac{\partial\left(c_t x_i\right)_k}{\partial t} = \frac{\partial J^n_{i,k}}{\partial z} \tag{3.2.14}$$

The mass balance equation used here is the equation (3.2.12) with i=1:

$$\frac{dn_{1,k}}{dt} = \left(J_{1,k-1} - J_{1,k}\right)A \qquad (3.2.15)$$

combined with the relationship between moles and mole fraction given by equation (3.2.13):

$$n_1 = c_t x_1 A \Delta z \qquad (3.2.16)$$

For a chosen value of the water velocity v_2, there are three unknowns: x_1, J_1, and n_1 and there are three equations. The system is fully defined.

Diffusion coefficients

According to Table 3.1.1, the diffusion coefficients in this model are:

$$Đ_{H+,water} = 9.3 \times 10^{-9}$$

$$Đ_{Cl-,water} = 2.0 \times 10^{-9}$$

Since this is a single electrolyte system, the diffusion coefficient of H^+ and Cl^- in water is calculated by equation (3.2.3a):

$$Đ_{12} = 2\left(\frac{1}{Đ_{H+,water}} + \frac{1}{Đ_{Cl-,water}}\right)^{-1}$$

Initial conditions

Initially, zero concentration is inside gel. In this case, the solution is already neutral electrically everywhere. Thus, it is not necessary to consider the neutrality of the solution as is done in the next model.

Secondly, HCl is treated as two separated ions: H^+ and Cl^-.

System model

Now, the system consists of three components: hydrogen ion (component 1), chloride ion (2) and water (3). And the water is chosen to be the reference component.

The MS equation

Since water is the reference frame and diffusion is only one dimension z, according to equation (3.2.2), the resulting MS equation for hydrogen and chloride ion in matrix form is:

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = -c_t \begin{bmatrix} \frac{x_2}{\mathcal{D}_{12}} + \frac{x_3}{\mathcal{D}_{13}} & -\frac{x_1}{\mathcal{D}_{12}} \\ -\frac{x_2}{\mathcal{D}_{12}} & \frac{x_1}{\mathcal{D}_{12}} + \frac{x_3}{\mathcal{D}_{23}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{\Delta x_1}{\Delta z} + x_1 z_1 \frac{\mathfrak{I}}{RT} \frac{\Delta \phi}{\Delta z} \\ \frac{\Delta x_2}{\Delta z} + x_2 z_2 \frac{\mathfrak{I}}{RT} \frac{\Delta \phi}{\Delta z} \end{bmatrix} \tag{3.2.17}$$

Transport equation

The mass balance equation used here for segment k is:

$$\begin{aligned} \frac{dn_1}{dt} &= \left(J_{1,k-1} - J_{1,k}\right)A \\ \frac{dn_2}{dt} &= \left(J_{2,k-1} - J_{2,k}\right)A \end{aligned} \tag{3.2.18}$$

combined with the relationship between moles and mole fraction in each segment given by equation (3.2.13):

$$\begin{aligned} n_1 &= c_t x_1 A \Delta z \\ n_2 &= c_t x_2 A \Delta z \end{aligned} \tag{3.2.19}$$

For a chosen value of the water velocity v_3, there are seven unknowns: x_1, x_2, J_1, J_2, n_1, n_2 and the implicit ϕ. However, there are only six equations. As described in section 3.2.3, under this circumstance, the index 2 problem appears. In order to solve the problem, an additional equation is needed to fully define the system, which is given by equation (3.2.8). In this case, it can be expressed as:

$$J_1 z_1 + J_2 z_2 = 0 \tag{3.2.20}$$

Boundary conditions for diffusion potential

When doing simulation, the boundary is set to zero on both sides. Later, it is found that it is more reasonable to set one side as zero diffusion potential with $\frac{\partial \phi}{\partial z} = 0$ on the same side. It will be discussed in Section 4.

Diffusion coefficients

The diffusion coefficients are the same as those used in the diffusion of HCl as one component.

Initial conditions

Initially, zero concentration is inside gel and the solution should be electrically neutral everywhere as described by equation (3.2.9):

$$\sum_i z_i x_i = 0 \tag{3.2.9}$$

In this case, it is

$$z_1 x_1 + z_2 x_2 = 0 \tag{3.2.21}$$

3.2.5 Diffusion of HCl and NaCl mixture

Now, it is the case of the diffusion problem in a multi-electrolyte system. The difference between this case and the previous one is that there is an additional ion, Na^+, in the system. According to Wesselingh and Krishna (2000), hydrogen chloride in water diffuses down its concentration gradient. So does sodium chloride. However, in the mixture of hydrochloric acid and sodium chloride, sodium might diffuse against its gradient, in the direction opposite to what we expect from Fick's law. This is caused by the electrical field generated by the H^+ ions of the HCl, which diffuse more rapidly than the others do.

System model

This system consists of four components: hydrogen ion (component 1), chloride ion (2), sodium ion (3) and water (4). Water is chosen to be the reference component.

The MS equation

Since water is the reference frame and diffusion is only one dimension *z*, according to equation (3.2.2), the resulting MS equation for the three components except water in matrix form is:

$$\begin{bmatrix} J_1 \\ J_2 \\ J_3 \end{bmatrix} = -c_t \begin{bmatrix} \frac{x_2}{\mathcal{D}_{12}} + \frac{x_3}{\mathcal{D}_{13}} + \frac{x_4}{\mathcal{D}_{14}} & -\frac{x_1}{\mathcal{D}_{12}} & -\frac{x_1}{\mathcal{D}_{13}} \\ -\frac{x_2}{\mathcal{D}_{12}} & \frac{x_1}{\mathcal{D}_{12}} + \frac{x_3}{\mathcal{D}_{23}} + \frac{x_4}{\mathcal{D}_{24}} & -\frac{x_2}{\mathcal{D}_{23}} \\ -\frac{x_3}{\mathcal{D}_{13}} & -\frac{x_3}{\mathcal{D}_{23}} & \frac{x_1}{\mathcal{D}_{13}} + \frac{x_2}{\mathcal{D}_{23}} + \frac{x_4}{\mathcal{D}_{34}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{\Delta x_1}{\Delta z} + x_1 z_1 \frac{\mathfrak{I}}{RT} \frac{\Delta \phi}{\Delta z} \\ \frac{\Delta x_2}{\Delta z} + x_2 z_2 \frac{\mathfrak{I}}{RT} \frac{\Delta \phi}{\Delta z} \\ \frac{\Delta x_3}{\Delta z} + x_3 z_3 \frac{\mathfrak{I}}{RT} \frac{\Delta \phi}{\Delta z} \end{bmatrix} \tag{3.2.22}$$

Transport equation

The mass balance equation used here has the same form as previously:

$$\begin{aligned} \frac{dn_1}{dt} &= \left(J_{1,k-1} - J_{1,k}\right)A \\ \frac{dn_2}{dt} &= \left(J_{2,k-1} - J_{2,k}\right)A \\ \frac{dn_3}{dt} &= \left(J_{3,k-1} - J_{3,k}\right)A \end{aligned} \tag{3.2.23}$$

Combined with the relationship between moles and mole fraction in each segment:

$$\begin{aligned} n_1 &= c_t x_1 A \Delta z \\ n_2 &= c_t x_2 A \Delta z \\ n_3 &= c_t x_3 A \Delta z \end{aligned} \tag{3.2.24}$$

For a chosen value of the water velocity v_3, there are ten unknowns: x_1, x_2, x_3, J_1, J_2, J_3, n_1, n_2, n_3 and the implicit ϕ. With this implicit ϕ, the additional equation is given by equation (3.2.8). In this case, it can be expressed as:

$$J_1 z_1 + J_2 z_2 + J_3 z_3 = 0 \tag{3.2.25}$$

Diffusion coefficients

The diffusion coefficients in this model are chosen from Table 3.1.1:

$$\mathcal{D}_{14} = 9.3 \times 10^{-9}$$

$$\mathcal{D}_{24} = 2.0 \times 10^{-9}$$

$$\mathcal{D}_{34} = 1.3 \times 10^{-9}$$

The diffusion coefficient of ion and ion pairs can be calculated by equation (3.2.3b).

$$Đ_{12} = \frac{Đ_{14} + Đ_{24}}{2} \frac{i^{0.55}}{\left|z_1 z_2\right|^{2.3}}$$

$$Đ_{23} = \frac{Đ_{24} + Đ_{34}}{2} \frac{i^{0.55}}{\left|z_2 z_3\right|^{2.3}}$$

where

$$i = 0.5\left(z_1^2 x_1 + z_2^2 x_2 + z_3^2 x_3\right)$$

$Đ_{13}$ can also be calculated with the same equation but with a negative sign.

Initial conditions

Initially, the solution should be electrically neutral everywhere as described by equation (3.2.9)

$$z_1 x_1 + z_2 x_2 + z_3 x_3 = 0 \qquad (3.2.26)$$

3.2.6 Diffusion of NaCl and NaOH mixture

Now, the mixture is changed to sodium chloride and sodium hydroxide as they are the solution used to remove milk fouling deposit. The system also consists of four components: chloride ion (component 1), sodium ion (2), hydroxide ion (3) and water (4). This system is similar to the previous one except that the common ion is sodium rather than chloride. Thus, the model equations are listed as follows without any explanations.

The MS equation

$$\begin{bmatrix} J_1 \\ J_2 \\ J_3 \end{bmatrix} = -c_t \begin{bmatrix} \frac{x_2}{Đ_{12}} + \frac{x_3}{Đ_{13}} + \frac{x_4}{Đ_{14}} & -\frac{x_1}{Đ_{12}} & -\frac{x_1}{Đ_{13}} \\ -\frac{x_2}{Đ_{12}} & \frac{x_1}{Đ_{12}} + \frac{x_3}{Đ_{23}} + \frac{x_4}{Đ_{24}} & -\frac{x_2}{Đ_{23}} \\ -\frac{x_3}{Đ_{13}} & -\frac{x_3}{Đ_{23}} & \frac{x_1}{Đ_{13}} + \frac{x_2}{Đ_{23}} + \frac{x_4}{Đ_{34}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{\Delta x_1}{\Delta z} + x_1 z_1 \frac{\Im}{RT} \frac{\Delta \phi}{\Delta z} \\ \frac{\Delta x_2}{\Delta z} + x_2 z_2 \frac{\Im}{RT} \frac{\Delta \phi}{\Delta z} \\ \frac{\Delta x_3}{\Delta z} + x_3 z_3 \frac{\Im}{RT} \frac{\Delta \phi}{\Delta z} \end{bmatrix} \qquad (3.2.27)$$

Transport equation

$$\begin{aligned}\frac{dn_1}{dt} &= \left(J_{1,k-1} - J_{1,k}\right)A \\ \frac{dn_2}{dt} &= \left(J_{2,k-1} - J_{2,k}\right)A \\ \frac{dn_3}{dt} &= \left(J_{3,k-1} - J_{3,k}\right)A\end{aligned} \tag{3.2.28}$$

The moles and mole fraction relationship

$$\begin{aligned}n_1 &= c_t x_1 A\Delta z \\ n_2 &= c_t x_2 A\Delta z \\ n_3 &= c_t x_3 A\Delta z\end{aligned} \tag{3.2.29}$$

The additional equation

$$J_1 z_1 + J_2 z_2 + J_3 z_3 = 0 \tag{3.2.30}$$

Diffusion coefficients

$$\mathcal{D}_{14} = 2.0\times 10^{-9}$$

$$\mathcal{D}_{24} = 1.3\times 10^{-9}$$

$$\mathcal{D}_{34} = 5.3\times 10^{-9}$$

The diffusion coefficient of ion and ion pairs can be calculated by equation (3.2.3b).

$$\mathcal{D}_{12} = \frac{\mathcal{D}_{14} + \mathcal{D}_{24}}{2}\frac{i^{0.55}}{\left|z_1 z_2\right|^{2.3}}$$

$$\mathcal{D}_{23} = \frac{\mathcal{D}_{24} + \mathcal{D}_{34}}{2}\frac{i^{0.55}}{\left|z_2 z_3\right|^{2.3}}$$

where

$$i = 0.5\left(z_1^2 x_1 + z_2^2 x_2 + z_3^2 x_3\right)$$

$\mathcal{D}_{13}$ can also be calculated with the same equation but with a negative sign.

Initial conditions

$$z_1 x_1 + z_2 x_2 + z_3 x_3 = 0 \qquad (3.2.31)$$

3.3 The complete model: diffusion through a gel

When diffusion happens in an electrolyte system containing a charged gel, things become much more complicated. Firstly, this model contains one more component than the electrolyte model: the polymer matrix and its fixed charges, and as a result, model parameters such as diffusivities increase in number. However, the knowledge of these parameters is still incomplete. Secondly, the influence of the gel charge on the diffusion process is complicated. The gel matrix with fixed charges often takes up an amount of counter-ions equivalent to the amount of fixed charges. This means that the internal electrolyte concentration is not a free parameter. Some of the solution is bonded by the matrix. In addition, water flux into or out the gel may cause it to swell or shrink. Thus, the volume change of the gel should be considered. Finally, there is the complexity of the mechanical properties of the gel. The water flux into the gel depends on the stiffness of the gel and the concentration of the external solution. And the stiffness depends on the type of gel and the degree of cross-linking. It should be noted that most protein gels are pH sensitive, which means electrical effects can be largely affected by the pH. This makes the diffusion problem even more difficult.

As I discussed before, an index 2 problem arose when solving the model equations of the electrolyte system. It was also the case of electrolyte-gel system. A lot of time had been spent on dealing with the MS equation with an implicit diffusion potential. As the research went forward, an augmented matrix method was found in the paper by Krishna (1987). It gave an explicit expression for diffusion potential and hence the diffusion equations can be solved. Oddly, this paper was not referenced in Taylor and Krishna (1993). Thus the model equations can be solved without the index 2 differentiation problem. When modelling diffusion of concentrated solutions the resulting equations can be considered to be the index 2 partial differential algebraic equations. They can be solved using the same method discussed in Section 3.2.

3.3.1 MS equation

The modelling starts from the same description of the generalised Maxwell-Stefan equation by Taylor and Krishna (1993). It has already been presented in Section 2.2.

$$\frac{x_i}{RT}\nabla_{T,P}\mu_i + \frac{x_i\overline{V}_i}{RT}\nabla P + x_i z_i \frac{\Im}{RT}\nabla\phi = \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i J_j^n - x_j J_i^n}{c_t Đ_{ij}} \tag{3.3.1}$$

This can be expressed in matrix form

$$\frac{1}{RT}\left(\mathbf{x}\cdot\nabla_{T,P}\boldsymbol{\mu} + \mathbf{x}\cdot\overline{\mathbf{V}}\nabla P + \mathbf{x}\cdot\mathbf{z}\Im\nabla\phi\right) = -\frac{1}{c_t}\mathbf{BJ} \tag{3.3.2}$$

where **B** is an *n*-1 square matrix with elements

$$B_{ii} = \sum_{j\neq i}\frac{x_j}{D_{ij}} \quad i = 1, n\text{-}1 \tag{3.3.3a}$$

$$B_{ij} = \frac{-x_i}{D_{ij}} \quad i \neq j \tag{3.3.3b}$$

The first term in equation (3.3.1) can be written as

$$\frac{x_i}{RT}\nabla_{T,P}\mu_i = \sum_{j=1}^{n-1}\Gamma_{ij}\nabla x_j \tag{3.3.4}$$

where

$$\Gamma_{ij} = \delta_{ij} + x_i\left.\frac{\partial \ln\gamma_i}{\partial x_j}\right|_{T,P,\Sigma} \tag{3.3.5}$$

Here γ_i is the activity coefficient and δ_{ij} equals one only when $i=j$. Thus equation (3.3.2) can be written for *n*-1 components as equation (3.3.6) which is a convenient form for solution

$$\boldsymbol{\Gamma}\nabla\mathbf{x} + \frac{1}{RT}\mathbf{x}\cdot\overline{\mathbf{V}}\nabla\mathrm{P} + \frac{\Im}{RT}\mathbf{x}\cdot\mathbf{z}\nabla\phi = -\frac{1}{c_t}\mathbf{BJ} \tag{3.3.6}$$

where $\boldsymbol{\Gamma}$ is a *n*-1 square matrix. In the case of an ideal solution, the activity coefficients are unity and $\boldsymbol{\Gamma}$ is an identity matrix.

It can be assumed that initially a system is electrically neutral everywhere

$$\sum_i z_i x_i(t_0) = 0 \tag{3.3.7}$$

and to retain neutrality there must be no net current:

$$\sum_i z_i J_i = 0 \tag{3.3.8}$$

Krishna (1987) combined equations (3.3.2) and (3.3.8) to give the augmented matrix from which J_i and $\nabla\phi$ could be determined.

$$\begin{bmatrix} -\frac{c_t}{RT}\left(\mathbf{x}\cdot\nabla_{T,P}\boldsymbol{\mu} + \mathbf{x}\cdot\overline{\mathbf{V}}\nabla\mathbf{P}\right) \\ 0 \end{bmatrix} = \begin{bmatrix} [\mathbf{B}] & [\mathbf{c}\cdot\mathbf{z}] \\ [\mathbf{z}] & 0 \end{bmatrix} \begin{bmatrix} [\mathbf{J}] \\ \frac{\mathfrak{I}}{RT}\nabla\phi \end{bmatrix} \tag{3.3.9}$$

During implementation of this, it was found necessary to scale the last row and column to ensure the matrix had a low enough condition number so could be solved without numerical errors. The profile of ϕ through a matrix can be determined by numerical integration of $\nabla\phi$ from a boundary condition of zero.

3.3.2 The pressure model

It is possible that diffusion could lead to a change in the volume of the gel. Swelling is easily added to the model by calculating the volume occupied by the water and ions associated with each fixed amount of polymer.

Pressure could be described by an equation relating the volumetric strain and a structural modulus of the polymer to pressure within it.

$$P = f\left(V/V_0\right) \tag{3.3.10}$$

where V is the volume of the gel and V_0 is the initial volume.

For one dimensional diffusion this might reduce to a thickness ratio. The function might take the form of equation (3.3.11).

$$P = G\left(\frac{V - V_{dry}}{V_{dry}}\right) \tag{3.3.11}$$

It is envisaged the G will depend linearly on the extent of cross-linking. According to Zrinyi and Horkay (1993) for a dry polymer network

$$G = RT\nu^* \tag{3.3.12}$$

where ν^* is the molar density of elastically active network chains. Here it was assumed that cross-linking is directly related to dissociation and a very simple relationship was used

$$G = 100(n_H) \tag{3.3.13}$$

where n_H is the number of undissociated sites per polymer. The value of 3000 for G was chosen arbitrarily in simulation.

3.3.3 The influence of pH

The ionic charge of a polyelectrolyte is likely to depend on the local pH, and this needs to be added to the dynamic model. For example, a protein in an alkali environment is expected to lose protons which will neutralise the hydroxyl ions. Normally this dissociation is considered to be at equilibrium but it is difficult to have dynamic diffusion of OH^- combined with instantaneous equilibrium of the same ion. In this case, a kinetic dissociation rate is proposed for dissociation of protons:

$$r_H = k_d\left(c_H^* - c_H\right) \tag{3.3.14}$$

where c_H is the molar concentration of undissociated protons, c_H^* is the concentration of undissociated protons in equilibrium with a given OH^- concentration, and k_d is a rate constant that is set sufficiently high so that the reaction is faster than any other process in the gel. For β-lactoglobulin the equilibrium concentration is given by Mercadé-Prieto et al. (2007b) as

$$c_H^* = c_{\beta lg}\sum_a A_a\left(\frac{1}{1+K_{d,a}c_{OH^-}}\right) \tag{3.3.15}$$

where the sum is over relevant amino acids in the protein. The constants A_a and $K_{d,a}$ represent the number of sites for each protein molecule and the dissociation constant for each amino acid are shown in Table 3.3.1 (Mercadé-Prieto et al., 2007b). For βLg the number of undissociated protons per molecule was found from equation (3.3.15) to be 36 at pH 7, reducing to 0 at high pH.

Table 3.3.1. Parameters for the βLg hydrogen ion equilibrium concentration

	Amino acid					
	His	Cys and α-NH_2	Tyr	Lys	Arg	Ser and Thr
A_a	2	2	3	14	3	15
$K_{d,a}$	$1x10^8$	$3x10^5$	$4x10^3$	$1.1x10^3$	30	6

3.3.4 A specific case: Diffusion of NaCl and NaOH

The model was applied to the multicomponent diffusion of NaCl, NaOH and water into and within a gel of β-lactoglobulin as studied by Mercadé-Prieto et al. (2007b). In this case, the system components were Na^+, OH^-, Cl^-, water and βLg. The first four components were free to diffuse relative to the βlg. The gel was considered to be a flat sheet with diffusion and hence swelling occurring in one dimension only.

Consider the one-dimensional diffusion into a flat gel immersed between two different solutions as shown in Figure 3.3.1. The gel can be divided into *m* layers or segments. Each segment could be considered to contain a fixed quantity of non-diffusing matrix material but there is no requirement that the volume (thickness) of each segment remains constant.

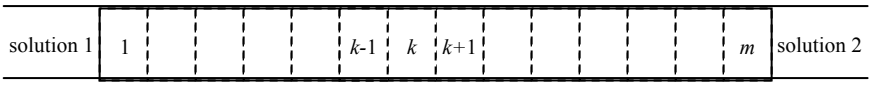


Figure 3.3.1. a one-dimensional model of a gel immersed between two solutions

Here the mass balance can be written for a finite segment

$$\frac{dn_{i,k}}{dt} = \left(J_{i,k-1} - J_{i,k}\right)A + V_k r_{i,k} \qquad (3.3.16)$$

where $n_{i,k}$ is the number of moles of species *i* in segment *k*, $J_{i,k}$ is the molar flux of *i* from segment *k* to *k*+1, V_k is the volume of segment *k*, and $r_{i,k}$ is the rate of generation of component *i* in the segment.

Both water and OH^- have non-zero rates of generation

$$r_{OH^-,k} = -r_{H_2O,k} = -r_{H,k} \tag{3.3.17}$$

Equation (3.3.16) can be solved using the "method of lines" (Schiesser, 1991) to solve for n_{ik} and hence x_{ik} for i = 1 to n-1 and k=1-m. The spatial gradients in equation (3.3.6) would be approximated by finite difference approximations and thus equation (3.3.6) becomes a set of algebraic equations.

Once n_{ik} is calculated at each time step, the volume of each segment can be found, P calculated from equation (3.3.11) and (3.3.13), and the position of the segments (Figure 3.3.1) can be recalculated.

Diffusion coefficients of ion-water have already been shown in Table 3.1.1. The empirical equation (3.2.3b) was used to calculate ion-ion diffusion coefficients:

$$D_{+,-} = \frac{D_{+,w} + D_{i,w}}{2} \frac{i^{0.55}}{\left|z_+ z_-\right|^{2.3}} \tag{3.2.3b}$$

where

$$i = 0.5 \sum_i z_i^2 x_i$$

The same equation applied for $D_{-,-}$ but with a negative sign.

3.4 Model solution method

Generally, the method of lines is applied to get the solution of the system (Schiesser, 1991). When this method is used, the gel (membrane) is equally divided into a series of small segments, and initially with a uniform composition. The flux is considered to happen at the boundaries between adjacent segments and the composition is evaluated as the average of adjacent segments.

The mole fraction gradient is evaluated as a first-order approximation:

$$\frac{dx}{dz} = \frac{x_{k+1} - x_k}{z_{k+1} - z_k}$$

The total concentration of each segment k is calculated by:

$$c_{t,k} = \frac{n_{t,k}}{V_k}$$

Where $c_{t,k}$ is the total concentration of segment k ; $n_{t,k}$ is the total moles in segment k and V_k is the volume of segment k.

For diffusion in electrolyte systems in Section 3.2, each volume of the segment is assumed constant during the diffusion. For the case of diffusion into and within β-lactoglobulin gel, the volume is initially set to be the same size, and during the diffusion swelling could happen. The volume of each segment was recalculated at each integration time step. It is assumed that ions take up no volume. It is also assumed that the polymer and water have constant densities.

For cases of diffusion in electrolyte systems (Section 3.2), the system equations were considered to be a partial differential algebraic equation system with a differentiation index of two and then they were solved using MATLAB ODE15S modified by Dr. Ken Morison. For the application to the gel (section 3.3), with an explicit expression for diffusion potential, the resulting equations were implemented in MATLAB directly using the built in ode solver ODE15S to solve the differential and algebraic equations together.

4 Results

Numerical results are presented for a number of cases and comparisons are made with solutions from literature and between different electrolyte systems.

4.1 Results of Bisschops' model

The dynamic model of Sephadex G-25 (Bisschop et al., 1988) has been introduced in Section 2.2.2. Since it is an example of using GMS approach in dynamic diffusion modelling, it is useful to reproduce the simulation as a testing study. The following figures show the simulation results. These figures (Figure 4.1.1 and Figure 4.1.2) were compared with the figures in the paper (Figure 5 and Figure 6), and it was confirmed that that the same results were obtained. This testing simulation yields information important for the research in this thesis, including: the dynamics of the swelling process of hydrogels can be successfully described on the basis of the generalised Maxwell-Stefan description and the model differential equation can be evaluated numerically by discretization in place and time.

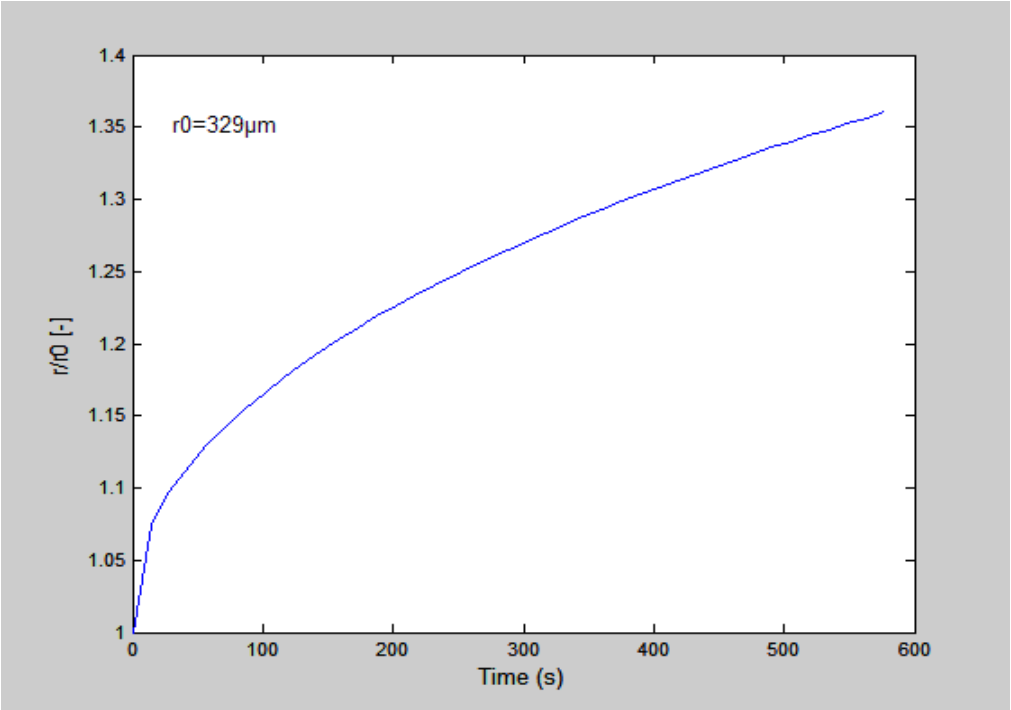


Figure 4.1.1. Solvent penetration during the swelling of Sephadex G-25

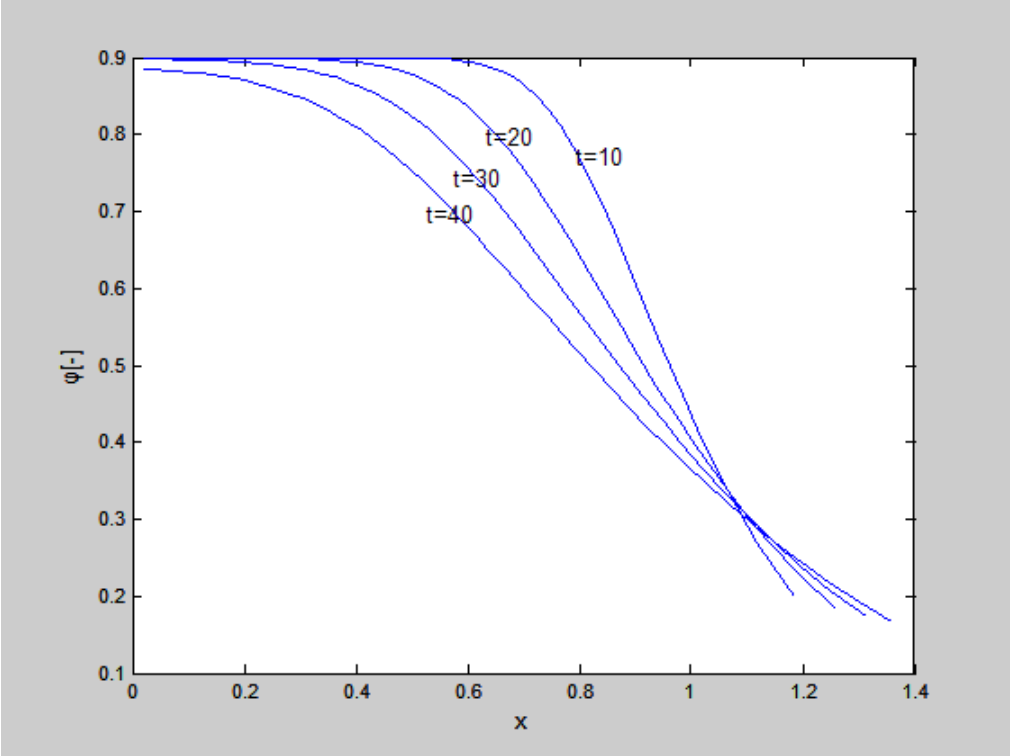


Figure 4.1.2. Concentration profiles in Sephadex G-25 gel particles. The curves indicate the polymer volume fraction as a function of the dimensionless radius at different times.

4.2 Results of HCl diffusion

As discussed before, if there is only one electrolyte in solution, its diffusion can be treated either as one component or as two ions. In the case of one component, the system is a one-component-diffusion system and thus the diffusion potential plays no role. In the case of two ions, the diffusion potential arises due to the interaction between the two ions.

The following figures show the results of two modelling approaches under the same condition. For the simulation the membrane thickness was set to 1 mm, and the boundary conditions were: the concentration of the left tank of the membrane was set to 0.018 mol/L, the right was set to 0. The volume of tank was set to 1 litre. Simulation time was 10 seconds. Initially, there was no solution inside the membrane. The axes employed have the same ranges to enable ease of comparison.

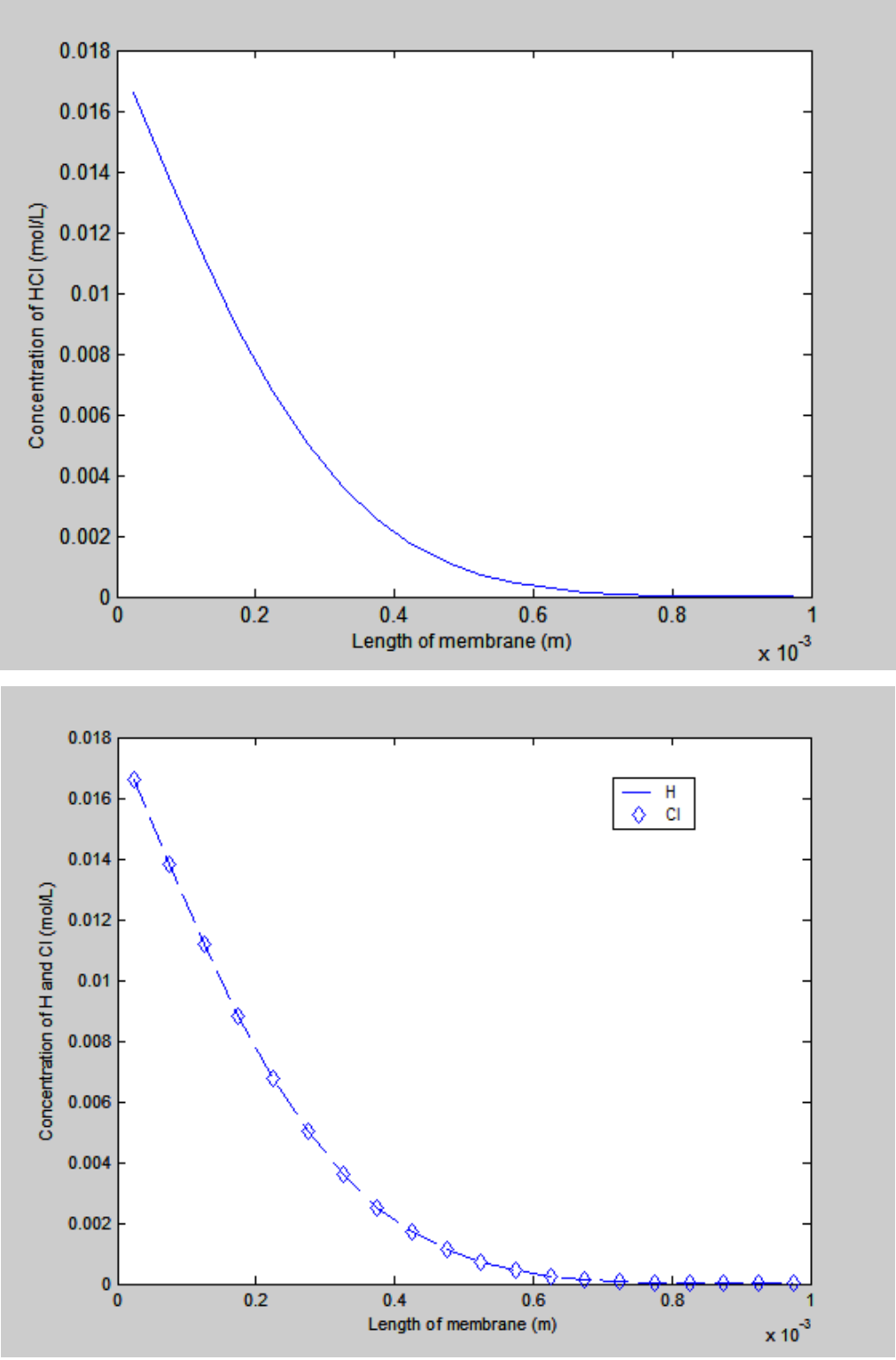


Figure 4.2.1. The concentration profile across the membrane.

Upper graph: HCl as one component. Lower: HCl as two ions

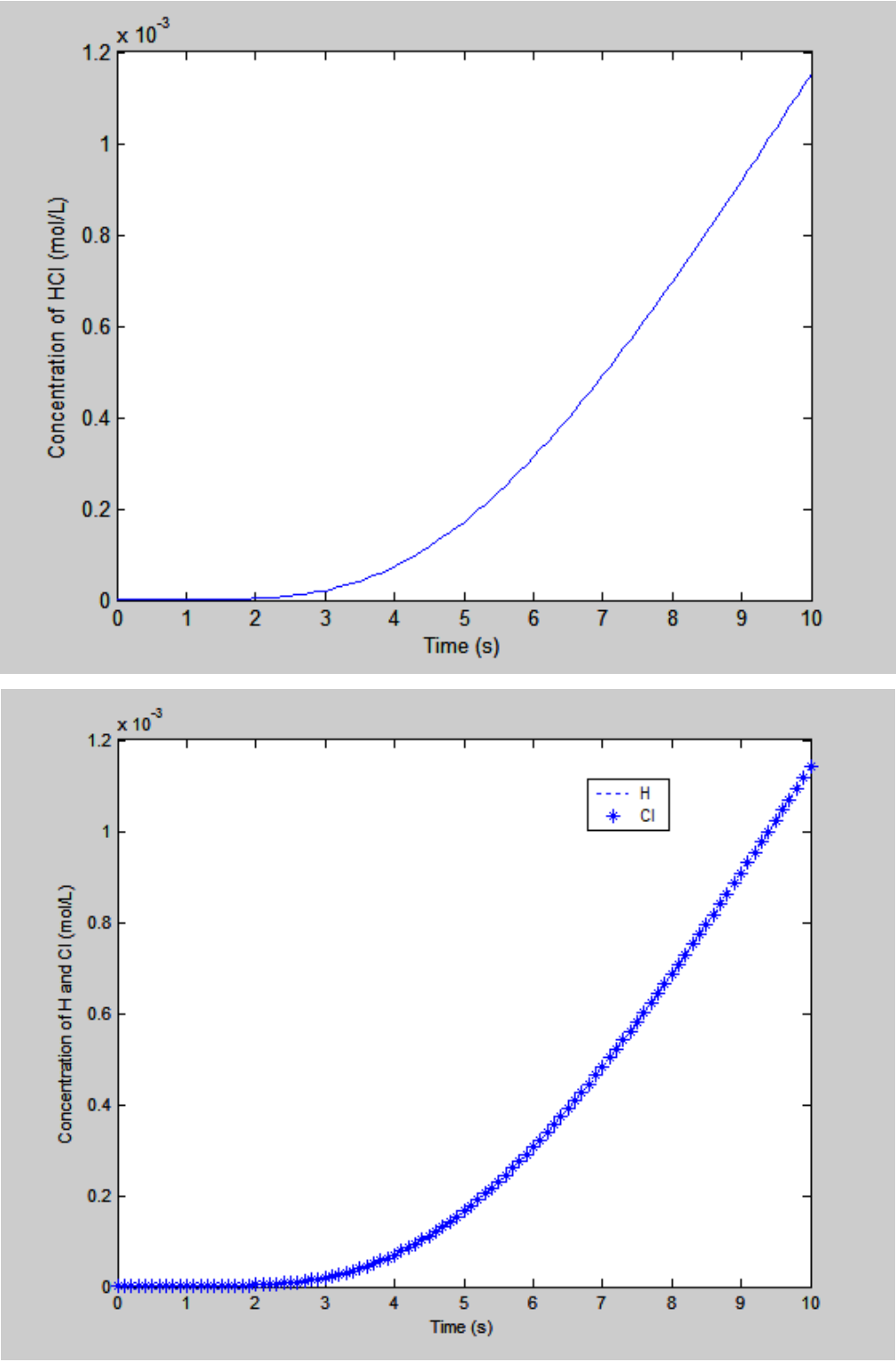


Figure 4.2.2. Concentration profile against diffusion time in the centre
Upper: HCl as one component. Lower: HCl as two ions

It is clear that both models produce the same results. Again, it demonstrates the success of the GMS approach as the basis of the diffusion modelling. Also, the index 2 differential equations were successfully solved to get the diffusion potential as shown in Figure 4.2.3.

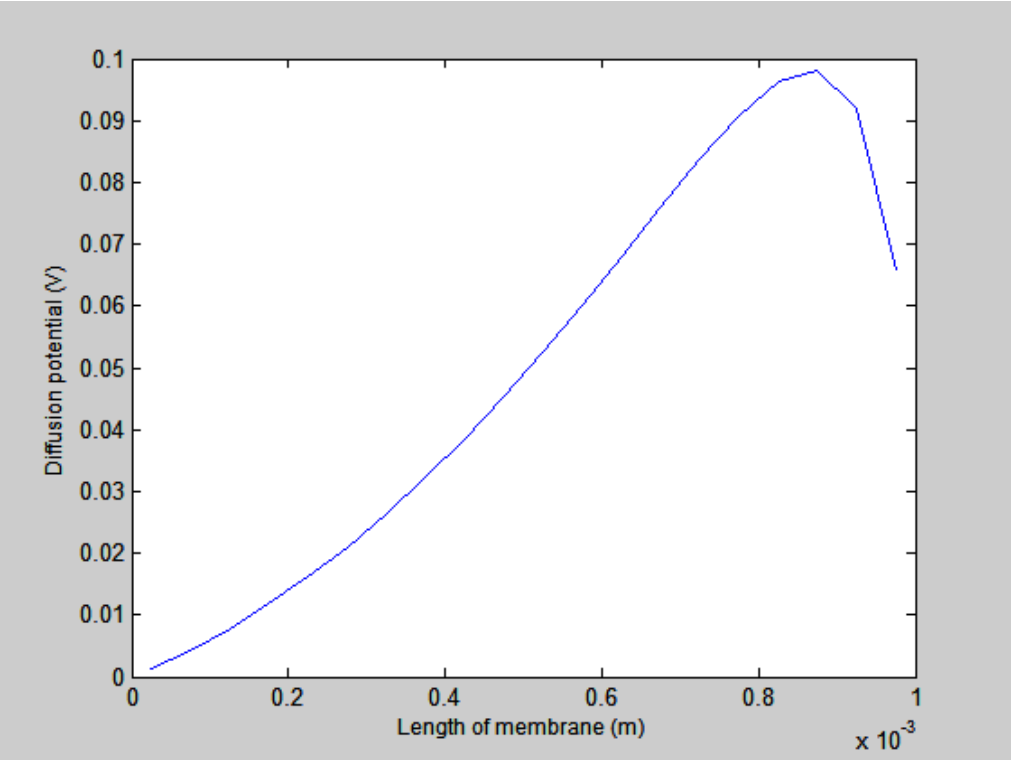


Figure 4.2.3. The diffusion potential across the membrane

The above results are also compared with Nernst-Planck solutions (Taylor and Krishna, 1993, Newman, 2004) shown in Figure 4.2.4 and Figure 4.2.5. As you can see, the concentration profile is the same (see Figure 4.2.1 and Figure 4.2.4), while the difference can be seen in diffusion potential (Figure 4.2.3 vs. Figure 4.2.5). The reason for this is that the diffusion potential of the model is bounded to zero at the right boundary but it is not in Nernst-Planck. It seems unreal that the diffusion potential on the right hand side of the membrane is set to zero. It can be improved by setting the value and derivative, $\partial\phi/\partial z$, to both be zero at one boundary. However, this was not done in the model in Section 3.2.4.

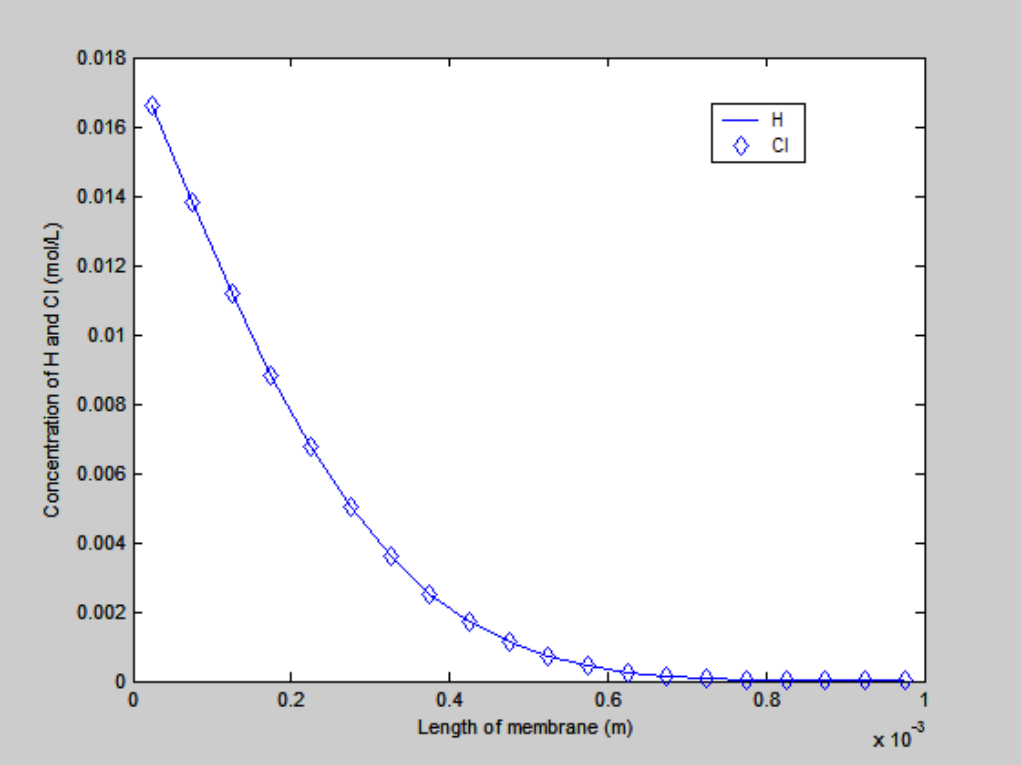


Figure 4.2.4. Concentration profile of Nernst-Planck

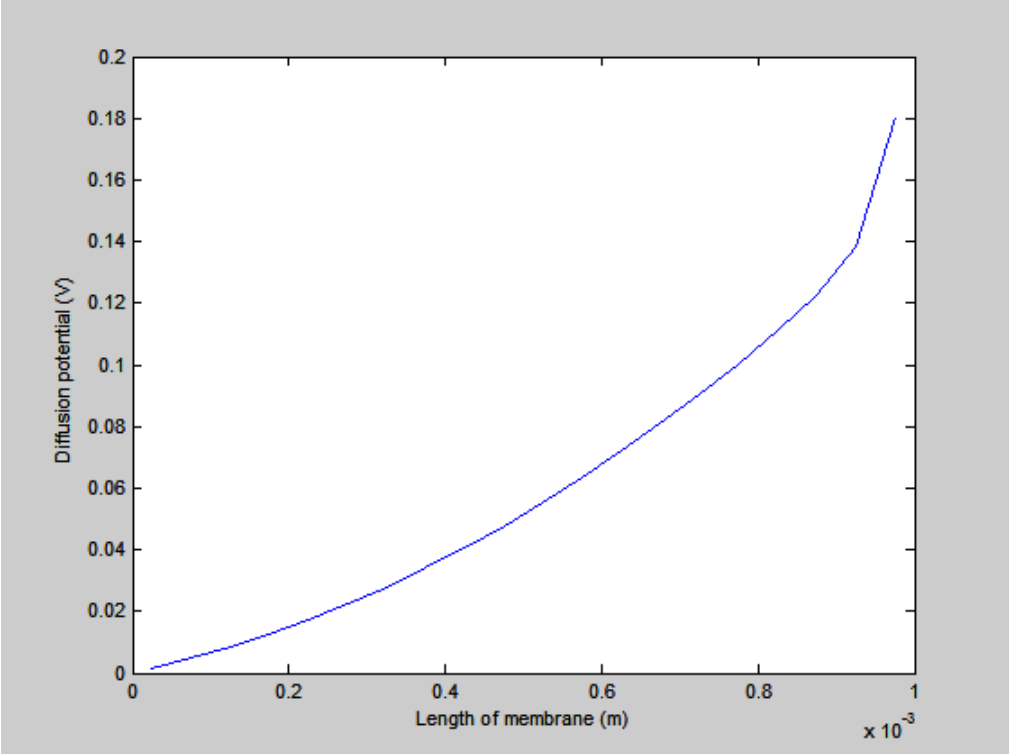


Figure 4.2.5. Diffusion potential of Nernst-Planck

4.3 Results of diffusion of HCl and NaCl

When a trace of NaCl is added to the HCl solution, three ions exist and they should diffuse separately. Several testing studies have been done to verify the model and solution.

In testing case one, the concentration of NaCl was set to zero and the other conditions were the same as those in Section 4.2. Simulation time was set to 10 seconds. Figure 4.3.1 shows the concentration profile of ions across the membrane. It is the same as that in Section 4.2., compared with Figure 4.2.1. The concentration of Na^+ is zero as the result of zero NaCl in the solution. Figure 4.3.2 and Figure 4.3.3 show the concentration in the centre segment of the membrane with different simulation times. Figure 4.3.4 shows the concentration of H^+ along the membrane with different simulation times. As can be seen, the concentrations become stable as the diffusion process goes on.

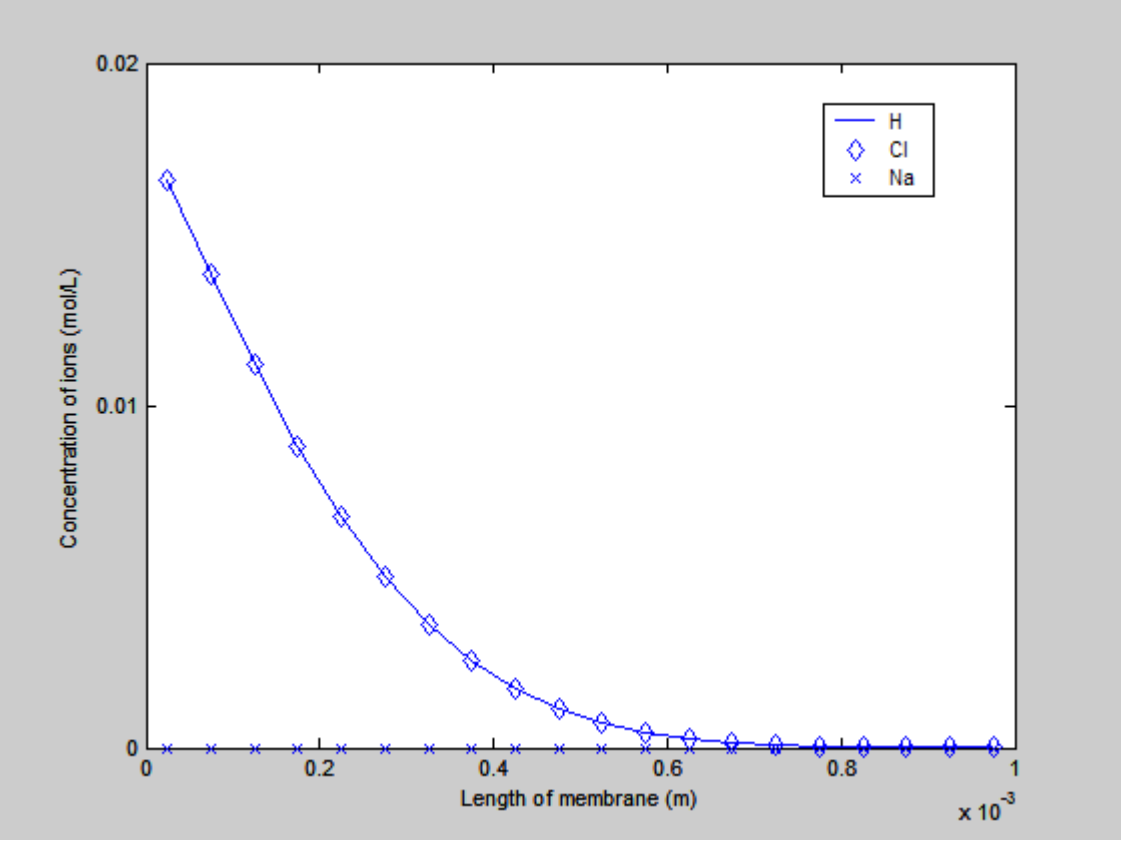


Figure 4.3.1. Concentration profile along the membrane after 10 seconds

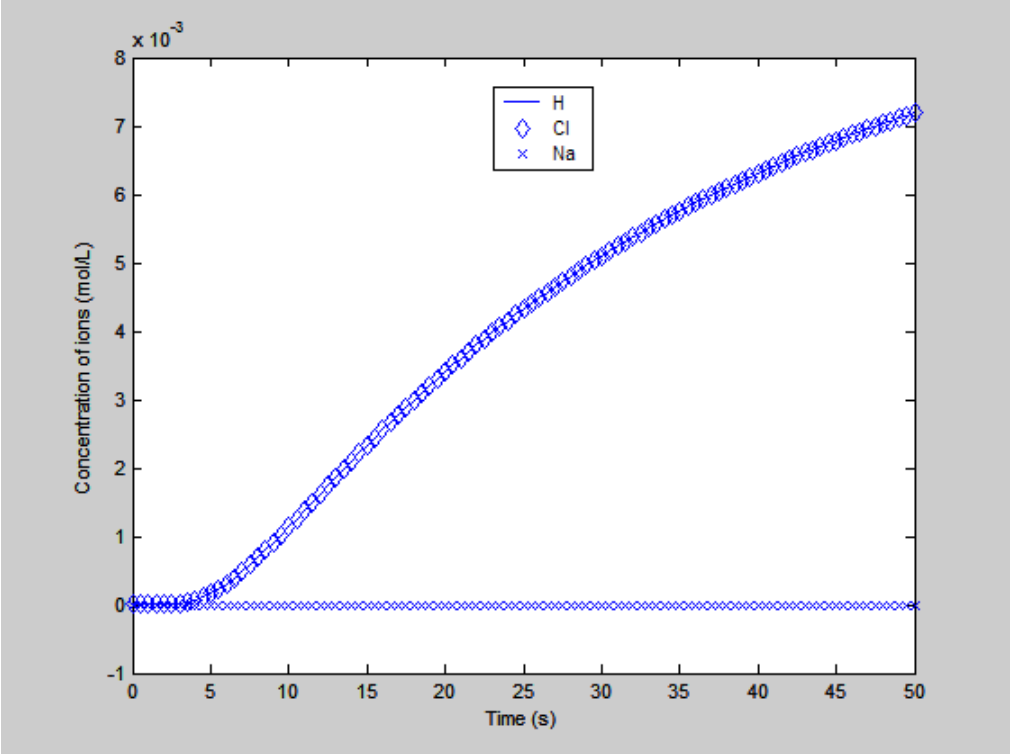


Figure 4.3.2. Concentration profile in the centre of the membrane after 50 seconds

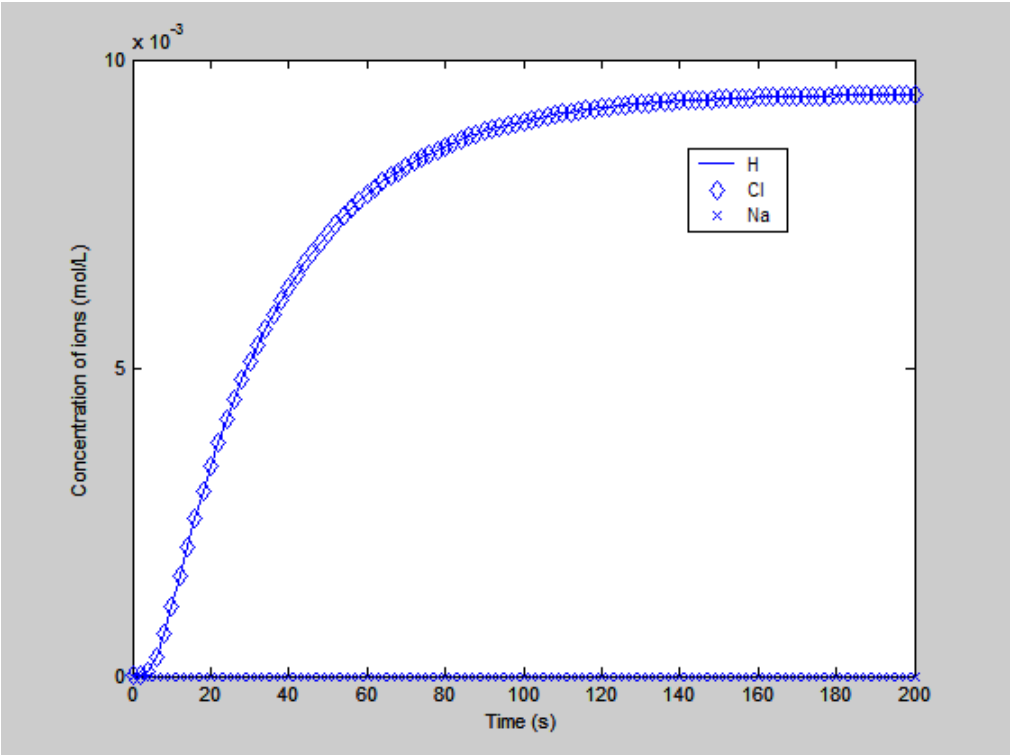


Figure 4.3.3. Concentration profile in the centre of the membrane after 200 seconds

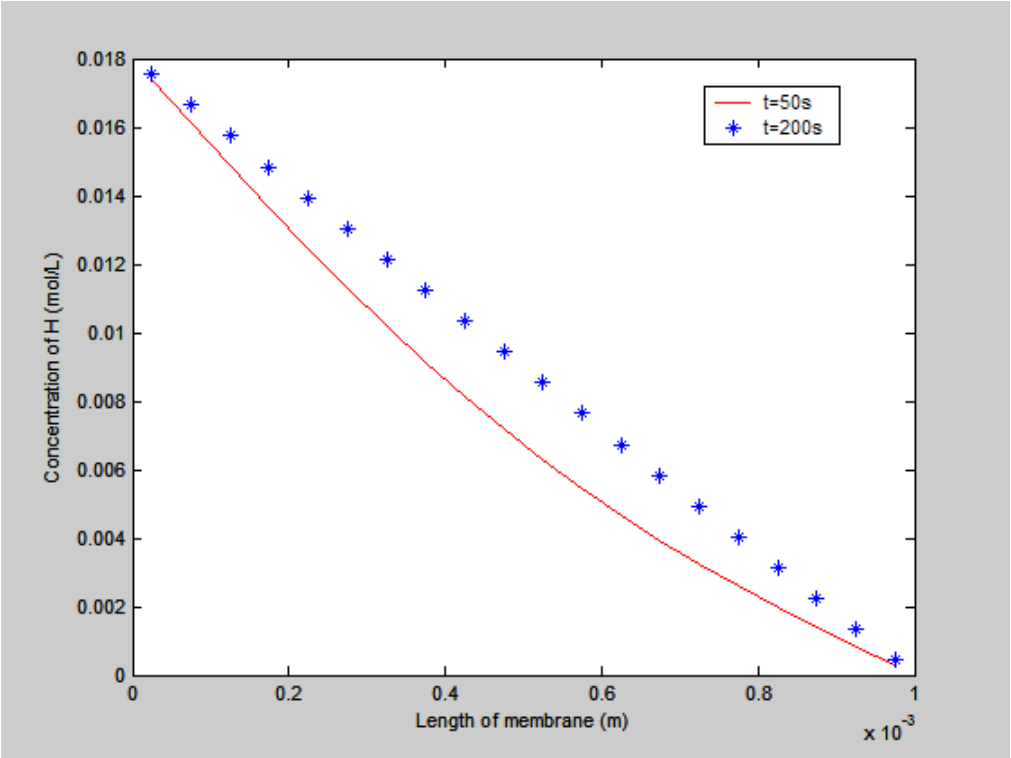


Figure 4.3.4. Concentration profile of H^+ at different time

In case two, a trace concentration of NaCl was added, other conditions were as follows:

- Initial conditions: no salt concentration (in order to avoid numerical errors, $1x10^{-8}$ was actually used rather than zero) inside the membrane.
- Boundary conditions: symmetry boundaries with HCl 0.03 mol/L and NaCl 0.01 mol/L on both sides of the tank.

The results are compared with those of the Nernst-Planck equation introduced in Section 2.2.3 (Taylor and Krishna, 1993, Newman, 2004) under the same condition. Figure 4.3.5 shows the concentrations compared with Figure 4.3.6, the result of the Nernst-Planck. Those two are almost the same. The small difference may due to the approximation of the Nernst-Planck, in which only the diffusion coefficients of solute/solvent are considered while the diffusion coefficients between ions are neglected.

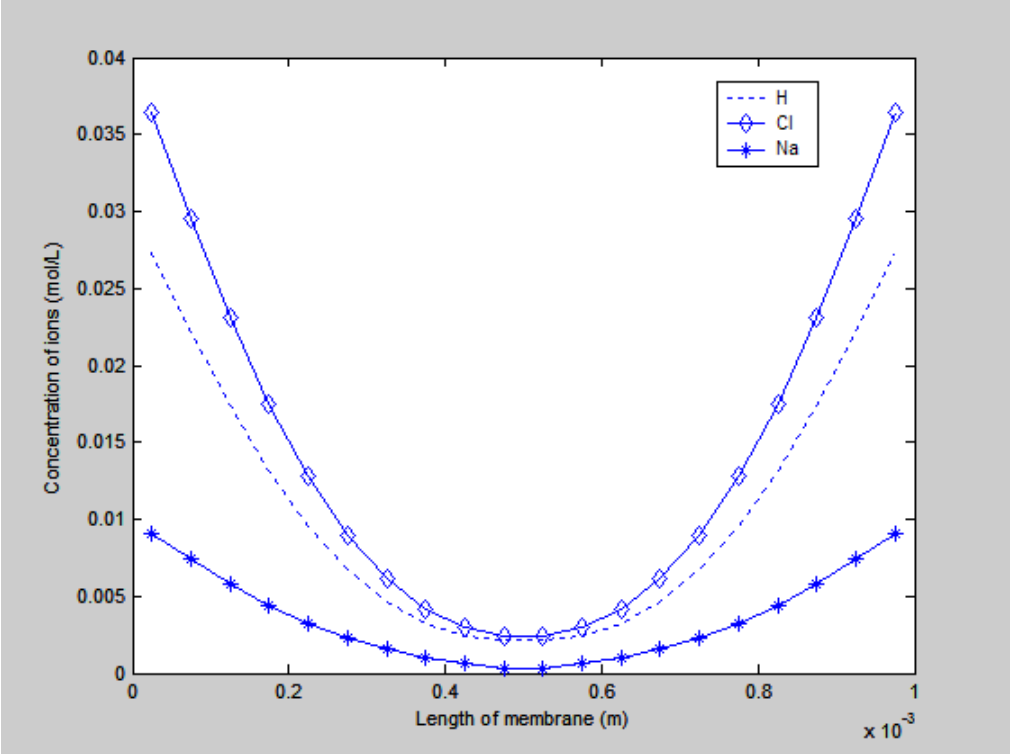


Figure 4.3.5. Concentrations along the length of the membrane after 10 seconds

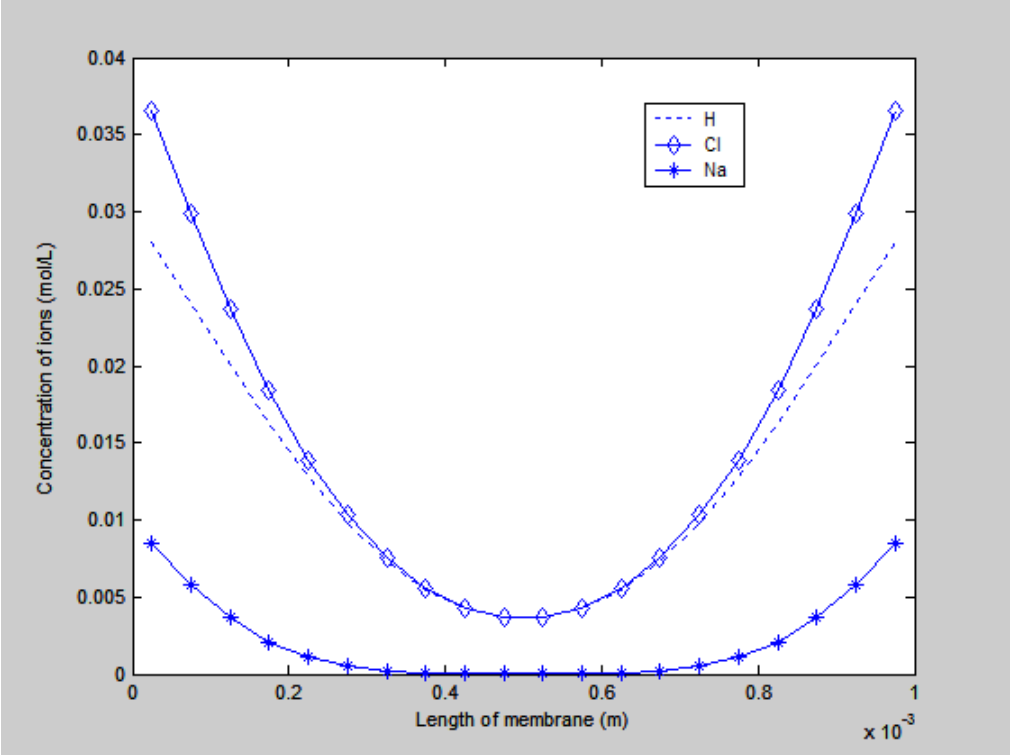
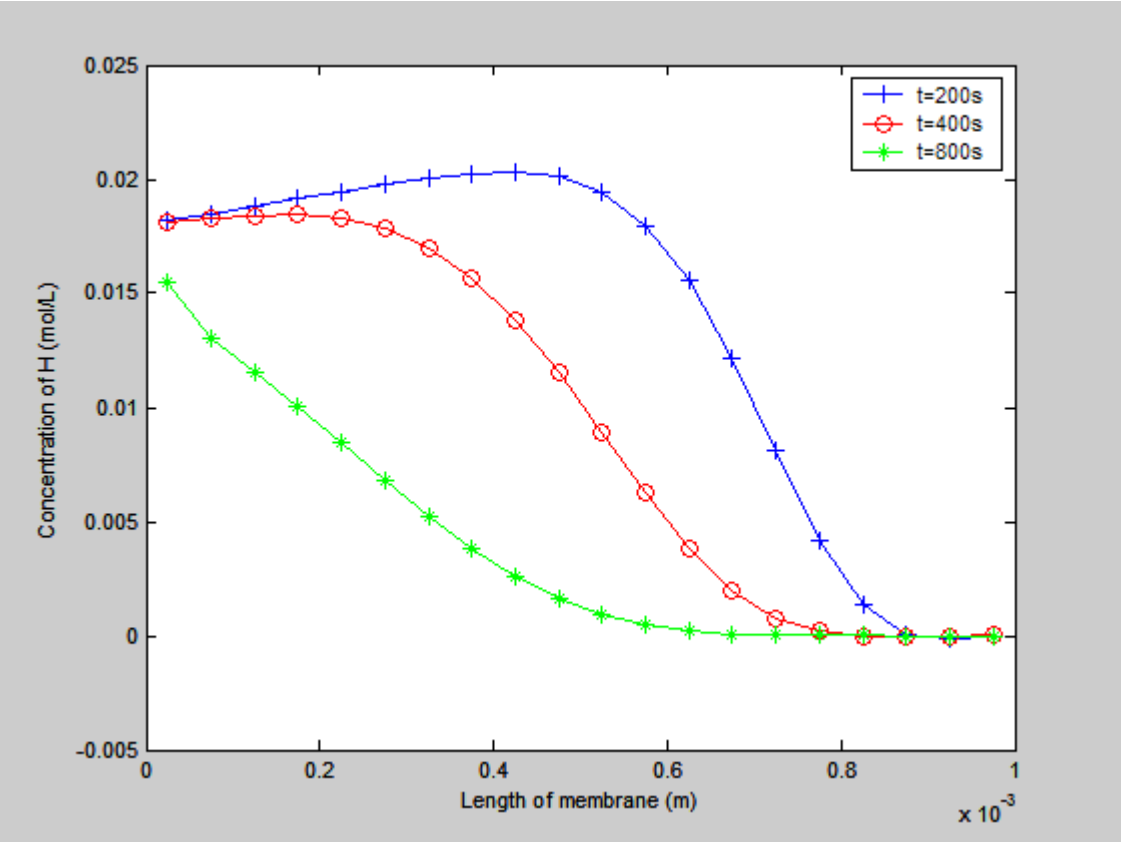


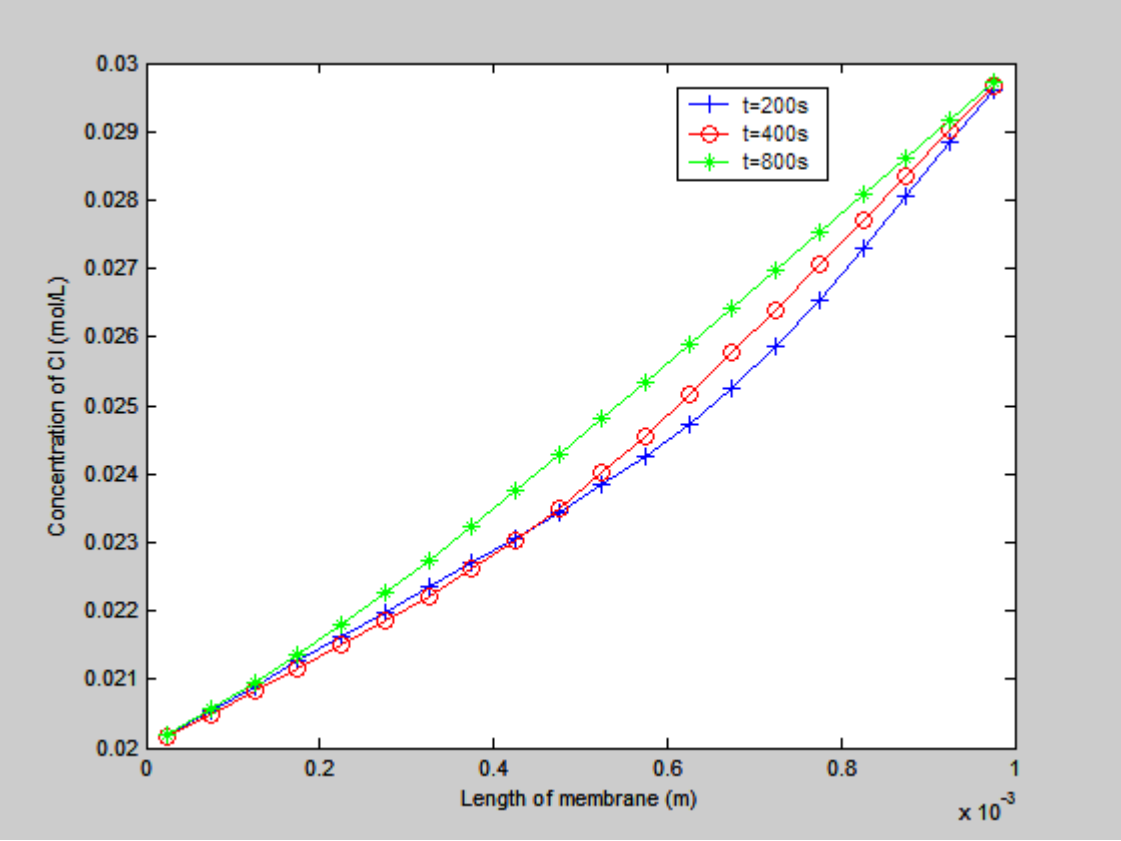
Figure 4.3.6. Concentrations of the Nernst-Planck equation after 10 seconds

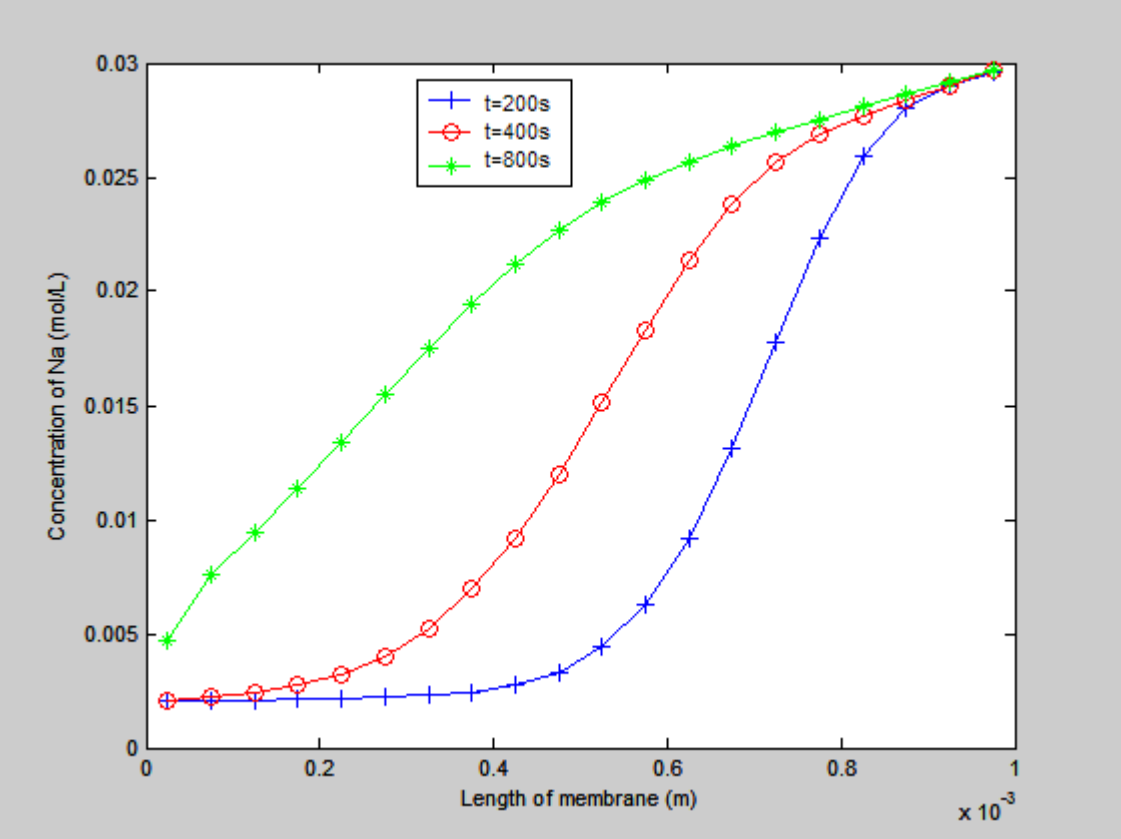
In the third case, a different initial and boundary condition was investigated.

- Initial conditions: there were 0.018 mol/L of HCl and 0.002 mol/L of NaCl inside the membrane.
- Boundary conditions: there were 0.018 mol/L of HCl and 0.002 mol/L of NaCl in the left tank and zero concentration of HCl and 0.03 mol/L of NaCl in the right tank.

Figure 4.3.7 shows that each ion diffuses separately. As the diffusion becomes steady, diffusion potential difference across the membrane becomes small. Figure 4.3.8 shows concentrations at centre segment of the membrane. The "inverse response" of H^+ is interesting but was not investigated further.




t=200s
t=400s
t=800s
Concentration of Cl (mol/L)
Length of membrane (m)
x 10^-3
0.03
0.029
0.028
0.027
0.026
0.025
0.024
0.023
0.022
0.021
0.02
0
0.2
0.4
0.6
0.8
1


t=200s
t=400s
t=800s
Concentration of Na (mol/L)
Length of membrane (m)
x 10^-3
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.2
0.4
0.6
0.8
1

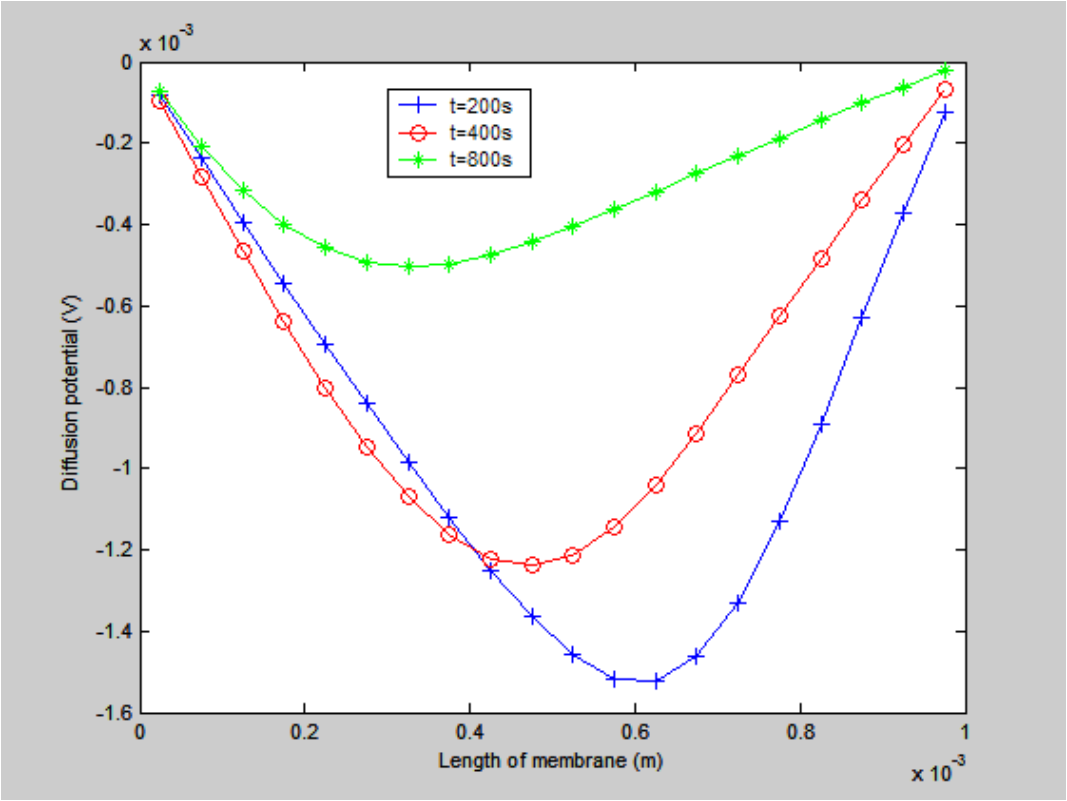


Figure 4.3.7. Concentrations and diffusion potential across the membrane at different times

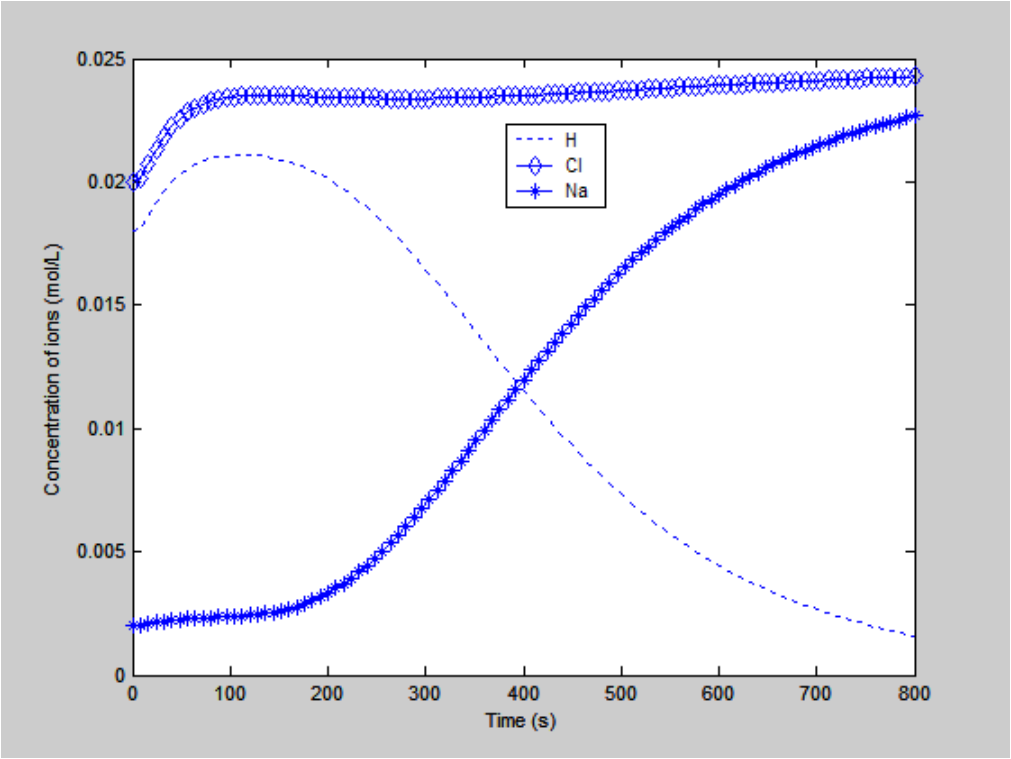


Figure 4.3.8. Concentrations in the centre segment of the membrane over 800 seconds

4.4 Results of diffusion of NaCl and NaOH

In this section, several different initial and boundary conditions were studied to see the influence on the diffusion process.

Both symmetrical boundary and asymmetrical boundary were considered. For symmetry, initially no concentration was inside the membrane. On both sides of the tank, the concentration of NaCl was 0.01 mol/L and it was 0.03 mol/L for NaOH. Figure 4.4.1 shows symmetrical diffusion with the concentration profile inside the membrane after 10 seconds.

For asymmetry, some salt concentration was inside the membrane before diffusion started. NaCl concentration was set to 0.02 mol/L and NaOH was none. On the left boundary, the concentration was equal to that inside the membrane. On the right boundary, NaOH was set high with 0.1 mol/L and NaCl was 0.01 mol/L. Figure 4.4.2 shows concentration profiles across the membrane. It shows that Na^+ and OH^- diffuse similarly while Cl^- diffuses differently. Figure 4.4.3 shows concentrations and diffusion potential at different simulation times.

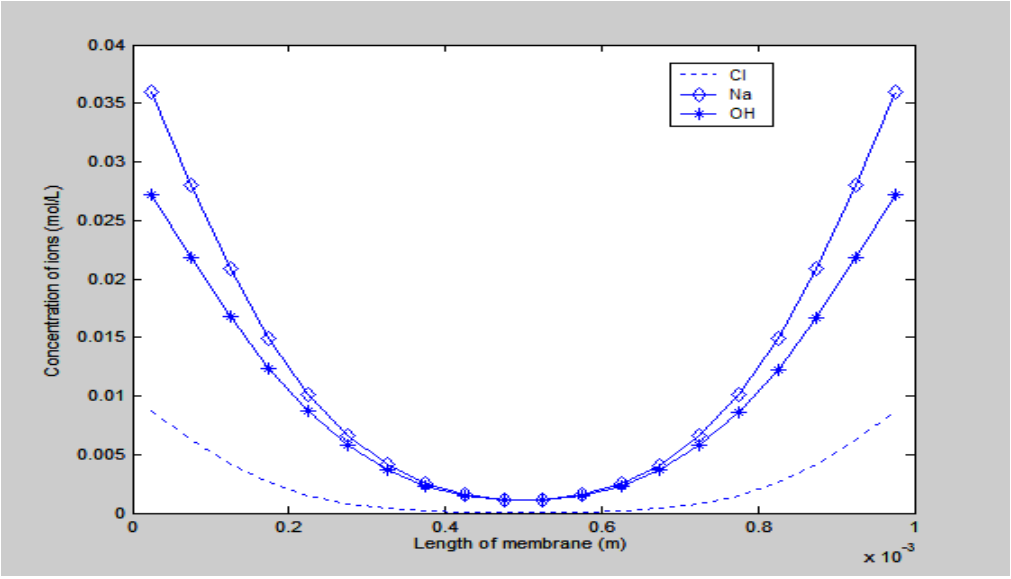


Figure 4.4.1. Concentration profile along the membrane after 10 seconds with symmetry boundary conditions

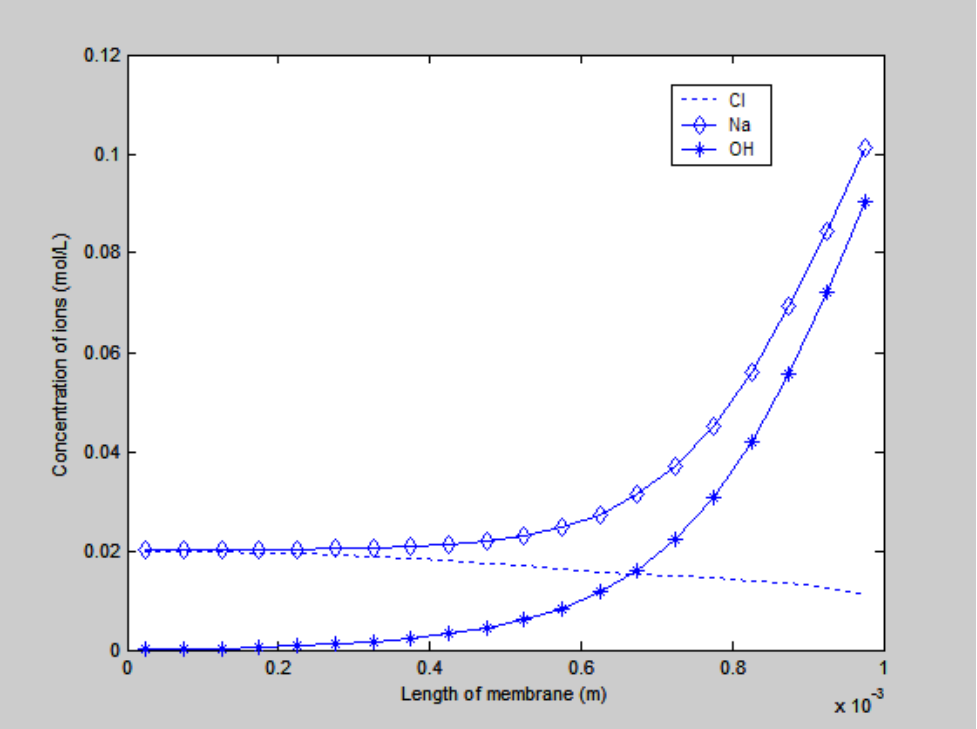
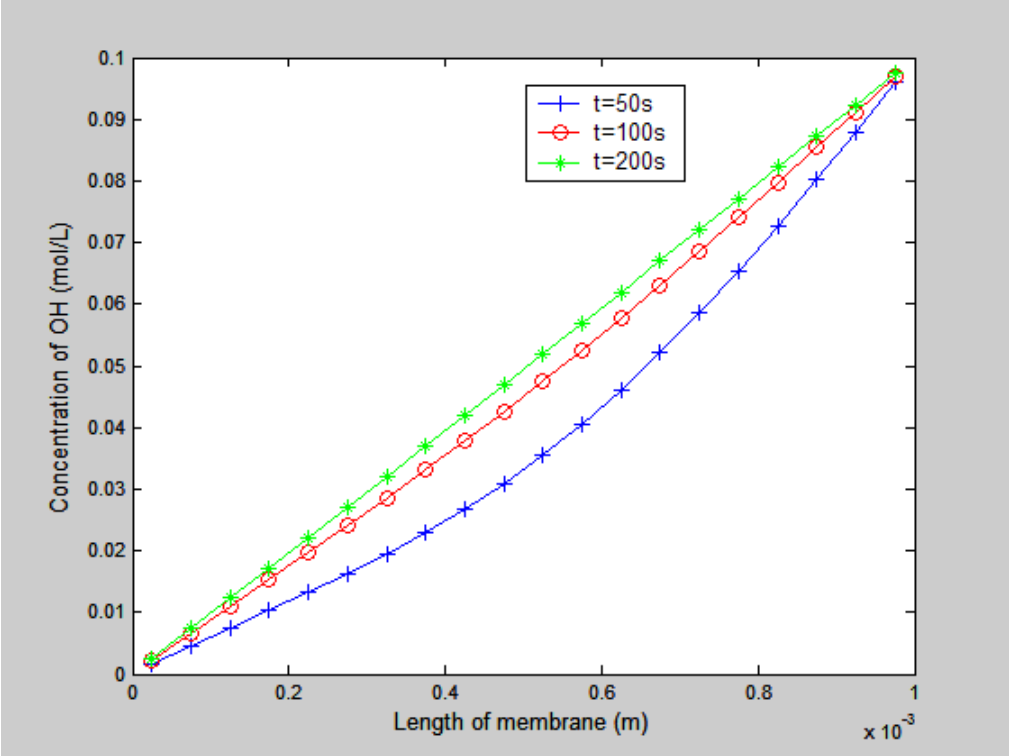
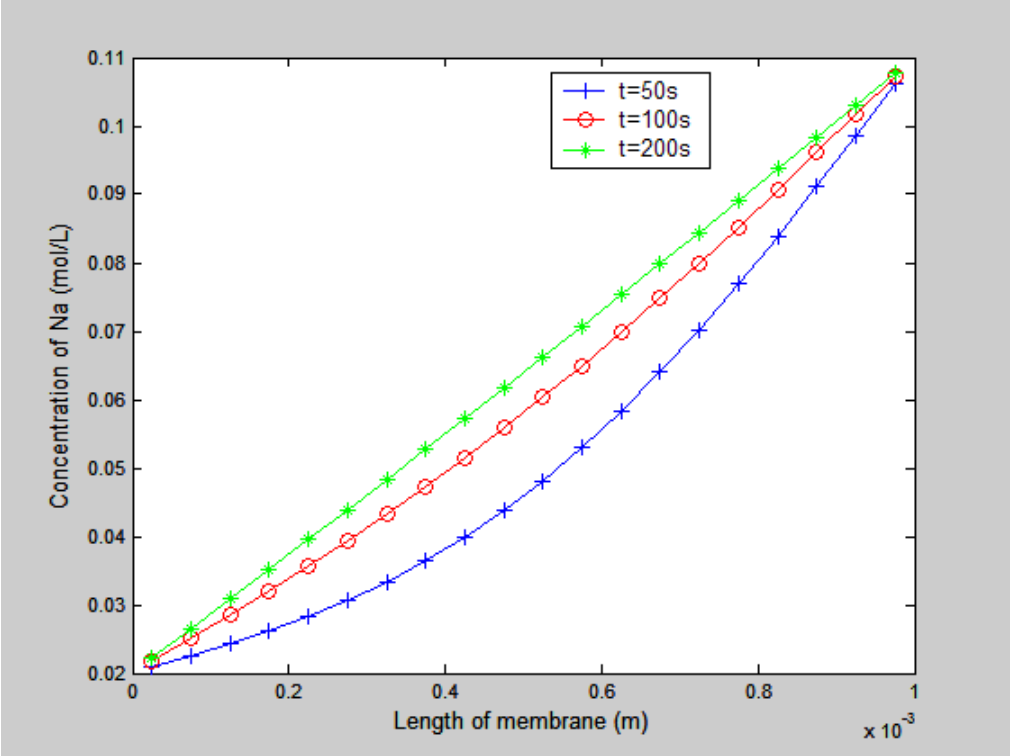
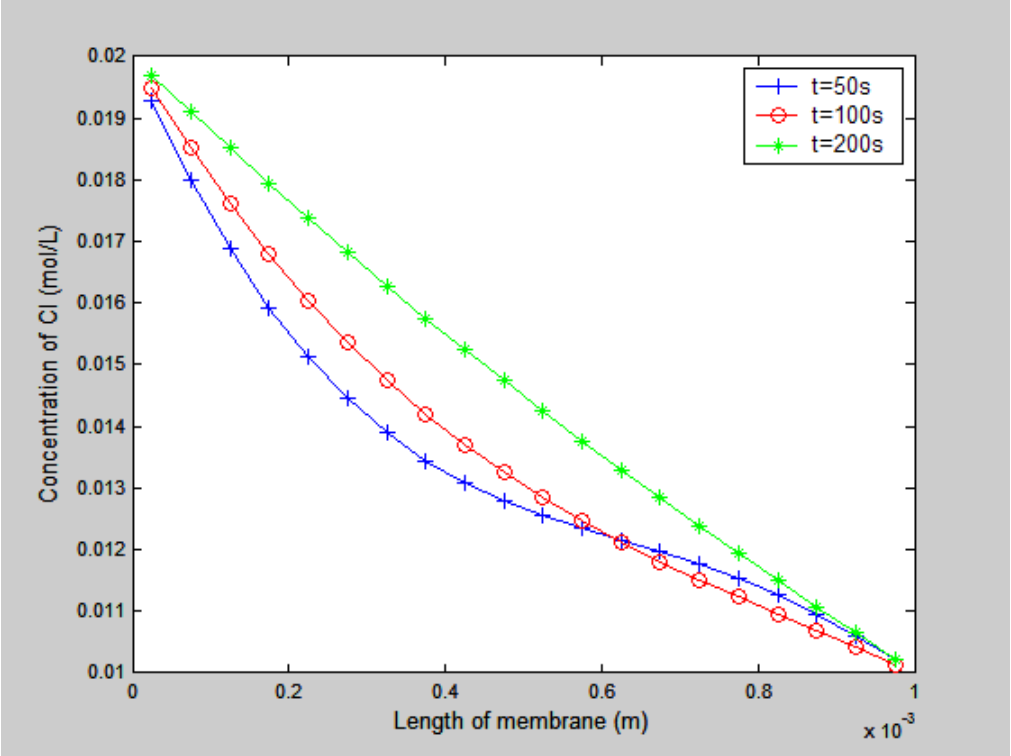


Figure 4.4.2. Concentration profile across the membrane after 10 seconds with asymmetry boundaries




t=50s
t=100s
t=200s
Concentration of Na (mol/L)
Length of membrane (m)
x 10^-3
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0
0.2
0.4
0.6
0.8
1


t=50s
t=100s
t=200s
Concentration of Cl (mol/L)
Length of membrane (m)
x 10^-3
0.02
0.019
0.018
0.017
0.016
0.015
0.014
0.013
0.012
0.011
0.01
0
0.2
0.4
0.6
0.8
1

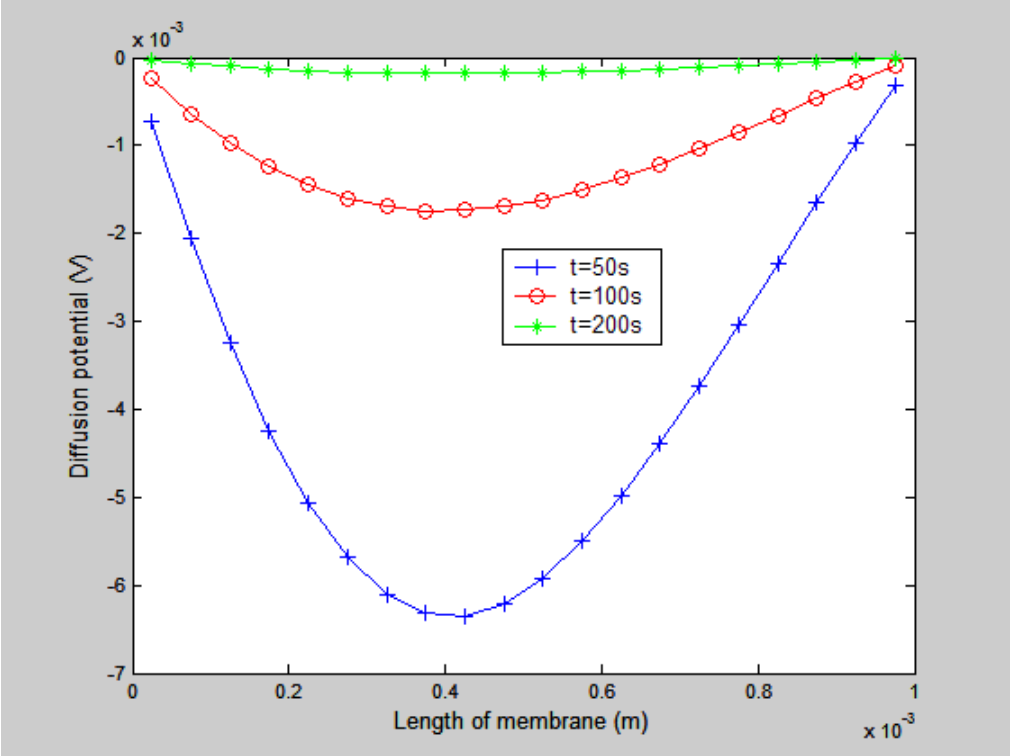


Figure 4.4.3. Concentrations and diffusion potential at different times

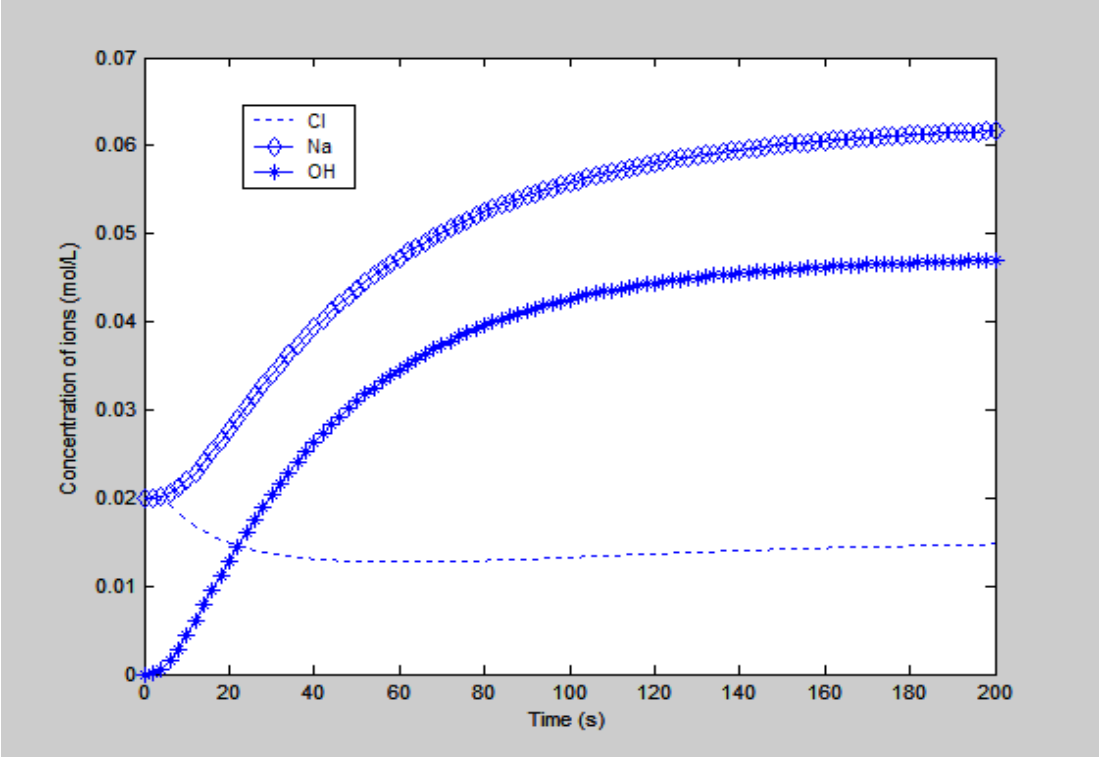


Figure 4.4.4. Concentration profile in the centre of the membrane against time

4.5 Results of diffusion of NaCl and NaOH with the gel

In this simulation, the initial thickness was set to 1 mm, the volume fraction of βLg was 10%. Its density was 1600 kg m^{-3} and molecular mass 18300 g/mol. The temperature was 25 ^{o}C. As the diffusion here involves the gel and water flux, the key issue is to investigate the swelling effect.

This model used very few assumptions. The *G* in the pressure equation (Equation 3.3.11) was the only component that was not determined *a priori*. Its value for 6% βLg gel at pH 5.4 was 3000 (Olsson, 2002). No claim is made that the equilibrium results are more accurate than those that might be obtained from an approach based on Flory-Huggins.

In this problem, initial and boundary conditions were as follows:

- Initial conditions: no NaOH concentration (in order to avoid numerical errors, $1x10^{-6}$ was actually used rather than zero) and a very small amount of NaCl concentration 0.00001 mol/L inside the membrane.
- Boundary conditions: symmetry boundaries with NaCl 0.135 mol/L and NaOH 1 mol/L on both sides.

Obtaining a solution using MATLAB's ODE15S was not always simple. The augmented matrix in the GMS equation had a very low condition number which caused numerical errors so it was scaled to obtain a condition number closer to one. This was done by multiplying the neutrality equation by 10^6 and by considering the potential to be in megavolts.

Further it was found that the initial concentrations of NaOH and NaCl within the gel had to be at least 10^{-6} and 10^{-5} mol/L to obtain a stable solution.

The modelling approach here has yielded results that are consistent with experimental observations. Water diffuses into the membrane as shown in Figure 4.5.1. The membrane swells until it reaches equilibrium (Figure 4.5.2). The model predicts that the swelling ratio will decrease with high NaOH concentration (Figure 4.5.3). This is

consistent with the experimental results in Mercadé-Prieto (2007b, Figure 3) shown as Figure 4.5.4. Interestingly, Figure 4.5.2 shows a sharp drop of membrane swelling ratio at the beginning of the diffusion. It happens very quickly and after that the membrane swells normally. The reason for this shrinkage may be the interaction between salt and water. At first few seconds the salt drags water out of the membrane and it leads to the sudden shrinkage of the membrane. Soon after that water diffuses back into the membrane and swelling appears.

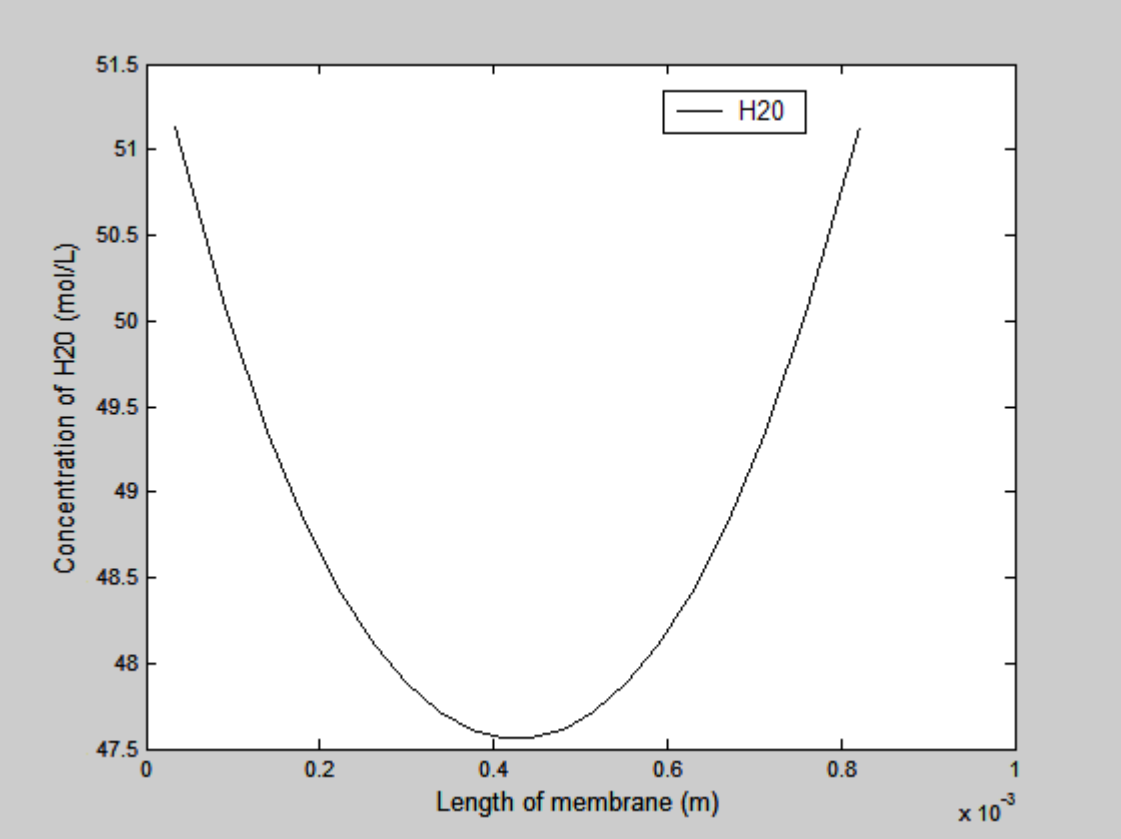


Figure 4.5.1. Concentration profile of H_2O across the membrane after 600 seconds

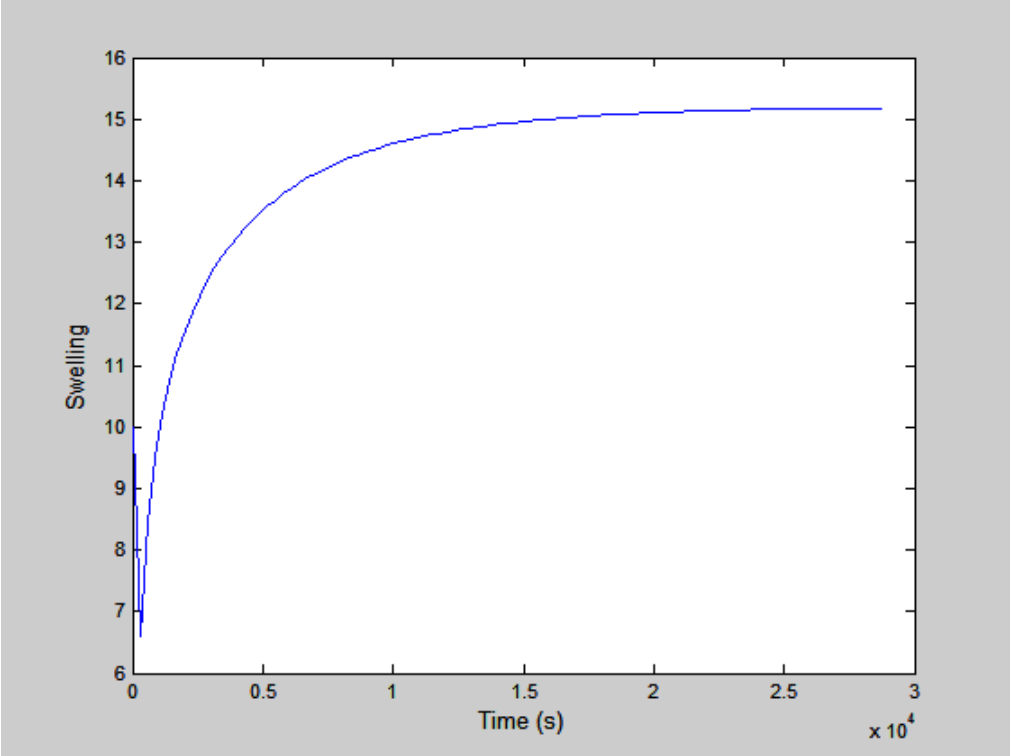


Figure 4.5.2. Swelling against time at [NaCl]=0.135mol/L and [NaOH]=1mol/L.

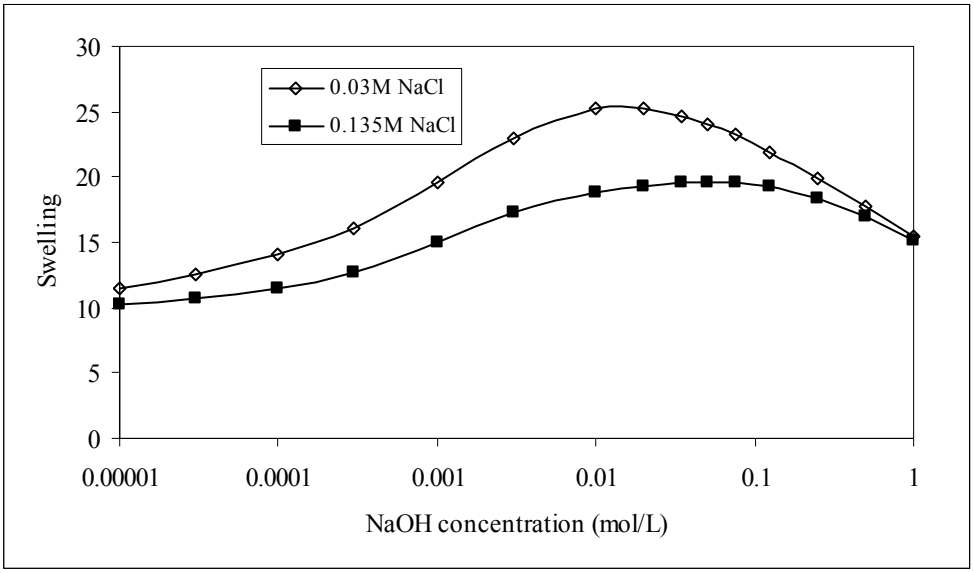


Figure 4.5.3. Swelling ratio vs. NaOH concentration.

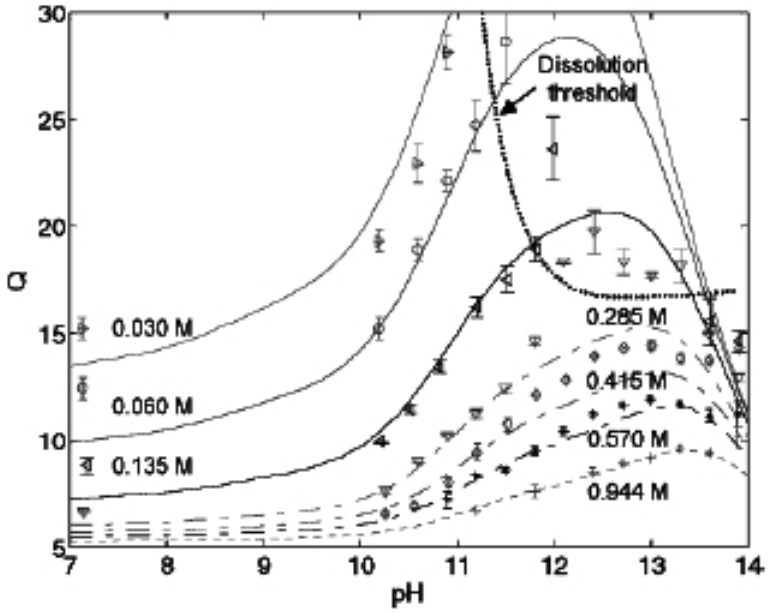


Figure 4.5.4. Effect of pH on the equilibrium swelling degree in βLg gels at different NaCl concentrations at 19 ^{o}C. Experimental points on the top right side of the dissolution threshold lines are for gels that started to dissolve before reaching swelling equilibrium. Error bars show standard error (Mercadé-Prieto, 2007b).

At this stage it was realised that there were numerous exciting results that could be obtained from the gel model. It was however decided that the main aims of the project had been achieved and that further interesting work should be carried out by others.

5 Discussion

The dynamic model of diffusion in electrolyte systems has been established on the basis of the generalised Maxwell-Stefan equations. It has been applied to both electrolyte and polyelectrolyte solutions. Numerical results of specific cases are presented and discussed in Section 4.

At this point, it was found that the Maxwell-Stefan formulation provides a very general and convenient approach for solving diffusion problems. It is a simple description as "driving force equals friction". The driving force can be easily generalised to explicitly include the contribution of the pressure gradient and the diffusion potential gradient. It avoids the Flory-Huggins equation when a gel is involved and gives a very good prediction. It can be extended to handle multicomponent diffusion problems as long as the diffusion coefficient for each pair is known.

The next step is to discuss the main features of the model.

Driving forces

The driving forces for diffusion in electrolytes were the chemical potential gradients of ionic species and the diffusion potential.

The chemical potential

The chemical potential gradients were taken at constant temperature and pressure. Effects of pressure were taken into account when a gel was involved in the diffusion. Non-ideality was not considered.

Ideality vs. non-ideality

The Maxwell-Stefan equation has the ability to deal with thermodynamic non-idealities. As discussed in Section 2.2.1, the matrix $\mathbf{\Gamma}$ describes the non-idealities of the solution. If the solution is ideal, $\mathbf{\Gamma}$ equals one. If the solution is non-ideal, activity coefficients are required. In the system containing electrolytes and gels, the activity coefficients include

activities of ions, solvent and the effect of polymer. There are several models to calculate ions and water activities in multielectrolytes. Pitzer's model has been fully presented in Section 2.2.5. Wesselingh and Krishna (2000) gave the Flory-Huggins (FH) thermodynamics model of the polymer effect on water activity. However, it is very difficult to define the activities in real simulation. Firstly, it is not clear how ionic and polymer effects should be combined to the solvent activity. Secondly, many parameters, like χ, are simply not available. The influence of the charge number of the gel on the activity of ions and solvent is not known. Finally, there are very few validations of the accuracy of such relationships. To avoid uncertain results, solutions were assumed ideal in this work. The results in Section 4 showed good agreement with experiments and literature. Therefore, non-ideality is not required to get diffusion behaviours.

Dilute and concentrated electrolytes

In dilute solution, the Nernst-Planck equation is often used to describe diffusion in electrolyte systems (Taylor and Krishna, 1993, Newman and Thomas-Alyea, 2004). In the application of diffusion of HCl, the solution of the Nernst-Planck equation was compared with that of the generalised Maxwell-Stefan equations and both yielded the same results. It demonstrates that the Nernst-Planck equation is only a limiting case of the generalised Maxwell-Stefan equations.

Diffusion potential

The diffusion potential is another contribution to the driving forces in the generalised Maxwell-Stefan equations. It is the electrostatic potential induced by diffusion of the ions. When there is a single pair of ions, there is no need to involve the diffusion potential as both ions move together to maintain electro neutrality. However, the diffusion potential becomes important when there are more than one species of either anion or cation in electrolyte systems. In the application of diffusion of electrolytes, the diffusion potential was implicitly defined and thus the MS equations were considered to be a partial differential algebraic equation system with a differentiation index of two and they were solved successfully with modified MATLAB ODE15S. However, as the research continued to make progress, an explicit expression for diffusion potential was

finally developed (Krishna, 1987) and the diffusion equations were solved for the diffusion of electrolytes in a gel.

Pressure

The pressure term in most models is obtained from the water equilibrium. This pressure is actually the osmotic pressure. According to Krishna (1987), the pressure term is very small and can be ignored in many cases. Therefore, in the application of diffusion in electrolytes, Krishna's assumption was followed. This gave quite good results. However, pressure cannot be ignored when swelling is considered. In the application of diffusion of NaOH and NaCl through a gel, the pressure term was a very simple model using Equations 3.3.11 and 3.3.13 to describe the elasticity of the polymer instead of Equation 2.2.15. The results were consistent with experimental observations. This demonstrates that the simple macroscopic description can give good results when dealing with problems in a molecular scope.

Diffusivities

The subject of multicomponent diffusion in polymers is not well developed. There is much on diffusivities of a single component in a polymer but much less on simultaneous diffusion of two or more components. Thus, the diffusivities used in the modelling are only estimates based on Wesselingh et al. (1995) and co-workers. The influence of the polymer structure on diffusivities is not considered. Wesselingh et al. (1995) estimated the tortuosity factor of diffusivities in polymers as

$$Đ_{ij}^{e} = \frac{1}{\varepsilon^{1.5}} Đ_{ij} \qquad (5.1)$$

with ε the void fraction of the polymer.

Equation (5.1) is also estimation and further investigation is required. As nobody has yet completely measured the diffusivities of multicomponents in polymers, Wesselingh and Krishna (2000) predict the phenomena using the free volume theory. Details of the free volume theory can be found in Wesselingh and Bollen (1997). The results which agree with experience show that the diffusivities are affected by swelling, mole fraction of the solvent, but not strongly. Thus, it is reasonable to neglect the polymer influence

on diffusivities at this moment and the numerical solutions agreed with experimental observations.

Swelling and Donnan equilibrium

Although the model used a simple equation to model the structure of a polymer gel, it predicted swelling behaviour of the gel and its equilibrium state. Some researchers (Wesselingh and Vonk, 1995, Bellara and Cui, 1998) provided the Donnan equilibrium description. This model gave a dynamic approach. No papers describing the dynamic approach to Donnan equilibrium were found during this project.

Numerical solutions vs. analytical solutions

The linearised theory and the effective diffusivity methods used to solve the generalised Maxwell-Stefan equations are not as useful as before because numerical solutions can be obtained successfully. However, they can still be useful to obtain less accurate results and for verification of numerical methods.

Future work

A simple, yet effective dynamic model of diffusion of electrolytes in gel has been established. However, it is only a good start and can be improved in many aspects. The study of swelling behaviour of a gel in electrolytes needs to be furthered. In the future, it would be good to research on the thermodynamics of solution and include non-ideality in the model. It would be also good to investigate the swelling of the gel and the effects of ionic forces, the pH and the concentration of the salt. Experiments are also needed to get more experimental observations.

6 Conclusions

The dynamics of diffusion of electrolytes in a protein gel were successfully described on the basis of the generalised Maxwell-Stefan description. The model presented was applied to several cases including electrolytes only and electrolytes with a gel. The model yielded differential equations that can be evaluated numerically by discretisation in place and time. The numerical solutions were obtained by using MATLAB ODE15S. Some conclusions can be made as follows:

1) The model was able to describe the dynamic behaviour of diffusion in electrolytes and it successfully predicted the swelling of the gel when a gel was involved.
2) The model successfully used diffusion coefficients from literature with one coefficient for each pair of components involved.
3) The model was applied to ideal solutions and this can be improved by adding thermodynamic factors and activity coefficients into the GMS equations.
4) It is not limited to gels with electrolytes. The model is also applicable to drug delivery system provided that the diffusion coefficients are available.
5) In contrast to earlier models, like Fickian diffusion model, the GMS model can be easily extended to mulicomponents.

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Appendix: Lists of MATLAB scripts

Table 1 below shows the MATLAB programming scripts used in this work and they are kept by my research supervisor Dr Ken R. Morison.

Table 1. MATLAB scripts

Diffusion models	MATLAB scripts
Diffusion of HCl as a single molecule:	SingleHCL.m
Diffusion of HCl as two ions	HCL.m
Diffusion of HCl and NaCl	HCLNa.m
Nernst-Planck solution to diffusion of HCl and NaCl	HCLNabook.m
Diffusion of NaCl and NaOH	CLNaOH.m
Diffusion of NaCl and NaOH through a gel	MSCleaning.m