Ultrafiltration of inorganic salts in the presence of polyelectrolytes

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Ultrafiltration of inorganic salts in the presence of polyelectrolytes

by

Polina Prokopovich

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of

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Abstract

In the present study Ultrafiltration (UF) of inorganic salts in the presence of a polyelectrolyte in the feed solution was investigated. Cellulose acetate membranes completely impermeable to the polyelectrolyte were selected with pore size 5-20 nm. At low concentrations of polyelectrolyte, a gel layer on the membrane surface does not form. At such low polyelectrolyte concentrations the concentration of inorganic salt in the permeate stream can be higher than in the feed solution. This salt concentration effect is the reverse of what is obtained with conventional membrane processes; where the permeate salt concentration is lower, or equal, to the salt concentration in the feed solution. It is shown that when ultra-filtering inorganic salts in the presence of a polyelectrolyte, the ratio of salt concentration in the permeate to feed is improved when the initial salt concentration in the feed solution is low. Concentration polarisation has a negative impact on this concentrating effect. A theory which elucidates the observed phenomenon has been developed and validated against experimental data. Polyelectrolyte charge, diffusion coefficient and other model parameters were found independently from experimental results and used to predict the ultrafiltration salt concentration in the permeate values. Filtration results were obtained with different inorganic salts such as $\text{KCl}$, $\text{NaCl}$, $\text{RbCl}$, $\text{CsCl}$, $\text{MgCl}_2$, $\text{KNO}_3$, $\text{K}_2\text{SO}_4$ using a water soluble polymer (poly(diallyl-dimethylammonium chloride) (PDDA)), and sodium borates (negative charged ions) in the presence of a poly(sodium-4-styrenesulfonate) (NaPSS).

**Key words:** nanofiltration, ultrafiltration, membrane separation, boron removal
The following publications have been published from this thesis:


N.V. Churaev, R.G. Holdich, P. P. Prokopovich, V. M. Starov, S. I. Vasin

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Nomenclature

Latin

\[ a = \frac{\delta}{D^+} \] model parameter characterises concentration polarisation influence

\[ b = \frac{c d h}{D_m} \] model parameter determined by hydrodynamic properties of the membrane

\[ c^0 \] total concentration of the polyelectrolyte in the feed solution

\[ c^- \] total concentration of anions in the feed solution

\[ c^+ \] total concentration of cations in the feed solution

\[ c_0^0 \] concentration of non-dissociated polyelectrolyte molecules

\[ c^1 \] total concentration of the polyelectrolyte inside concentration polarization region

\[ c^1_i (0-) \] concentration of anions on the membrane surface from volume side

\[ c^1_i (0+) \] cation concentration on the membrane surface from volume side

\[ c_g \] concentration of gel formation

\[ c_i^0 \] concentration of the polyelectrolyte with \( i \) dissociated sites

\[ c_m^1 \] concentration of the polyelectrolyte on the membrane surface

\[ D \] total diffusion coefficient of the polyelectrolyte

\[ D_- \] diffusion coefficient of an anion

\[ D_+ \] diffusion coefficient of a cation

\[ D_i \] diffusion coefficients of the polyelectrolyte ions

\[ D_m \] diffusion coefficient of ions inside the membrane

\[ e \] electron charge

\[ f_{\text{max}} \] maximum of \( f \) function corresponding to the optimum filtration velocity \( \nu_{\text{opt}} \)

\[ g = \gamma - 1 \] model parameter determined by physical properties of the membrane and salts

\[ h \] membrane active layer thickness

\[ i \] number of dissociated sites

\[ k \] Boltzmann constant
$K_m$  permeability of the active layer of the membrane

$k_p$  dissociation reaction constant

$K_p$  association reaction constant

$j_i$  fluxes of dissociated polyelectrolyte ions

$j_-$  flux of anions

$j_+$  flux of cations

$l$  thickness of the gel layer

$N$  number of chains of polyelectrolyte molecules

$p$  probability

$Pe$  outer Peclet number

$Pe_0$  dimensionless pressure

$Pe_m$  dimensionless filtration velocity

$q$  reaction rate

$R$  rejection coefficient

$T$  absolute temperature

$v$  filtration velocity

$z^0$  average value of dissociated sites in the feed solution

**Greek**

$\bar{\alpha}$  coefficient, considering the difference in the convective flow of the molecules of the dissolved substance from the rate of water transfer in the membrane

$\beta_-$  deviation of the average convective velocity of anions from the filtration velocity of water inside the membrane

$\beta_+$  deviation of the average convective velocity of cations from the filtration velocity of water inside the membrane

$\gamma$  distribution coefficient which is a ratio between the ion concentration in the bulk and inside a membrane pore

$\Delta p$  pressure drop across the membrane

$\Delta p_{cr}$  critical pressure drop

$\Delta \Phi^0$  electric potential jump across the membrane surface
\( \delta \) thickness of the boundary layer
\( \Phi_+ \) potential of specific interactions of ions with the membrane materials
\( \Lambda \) degree of concentration
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CHAPTER 1: \textit{INTRODUCTION}

In this work a new approach is presented for separation of low-molecular weight components by concentrating them in the permeate stream using a polyelectrolyte in the feed solution during Ultrafiltration processes. Different inorganic salts were used such as $\text{KCl}$, $\text{NaCl}$, $\text{RbCl}$, $\text{CsCl}$, $\text{MgCl}_2$, $\text{KNO}_3$, $\text{K}_2\text{SO}_4$ with a mixture of a water soluble polymer (poly(diallyl-dimethylammonium chloride) (PDDA)), and sodium borates (negative charged ions) in the presence of a poly(sodium-4-styrenesulfonate) (NaPSS). The present study offers a less expensive and more efficient way of concentrating inorganic ions as compared with conventional RO/NF methods. The method is applicable to all anions and cations and has applications where removal of low concentration ions is required. This can be found in the nuclear industry, boron removal/recovery and drinking water purification.

Today obtaining water suitable for drinking as well as for industries is becoming a bigger challenge. Despite the improved performance of currently available processes for drinking water, low cost treatment is still a major need in many developing countries in Africa and Asia. Also, water purity is becoming more and more stringent in industrial processes such as electronic and pharmaceutical. In the food and pharmaceutical industries, it is necessary to extract the concentrate of the useful component from the solution. For example, in the pharmaceutical industry medicines are obtained in the form of aqueous solutions, containing only a portion of the desired product, which must be obtained finally in the form of a powder. The common process of evaporation is little help here, because the required products lose their chemical properties with an increase in temperature (thermal degradation), therefore it is necessary to use only expensive vacuum evaporation. The consequence of these challenges is a demand for new separation techniques.

Particular attention has been recently posed on the removal of boron, this element contaminates natural waters around the world. In relatively small amounts it is essential for plant growth, but becomes toxic when its concentration exceeds a critical value of 0.5 ppm (WHO, 1998). The increase use of boron in industrial processes causes an increased concentration in the environment reaching or exceeding the recommended limit suggested by World Health Organisation (1998).
The separation and concentration of radionuclides is important in the nuclear industry and Cesium 137 is most widely used radioisotope (EPA, 2006), it is also used in the radiotherapy of cancer. Due to the its radioactivity the presence of this element in water and soil is a serious danger to living creatures, consequently the amount of Cesium 137 is strictly regulated both by Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission.

Filtration can be defined as the separation of two or more components from a fluid stream. In conventional usage, it usually refers to the separation of solid, immiscible particles from liquid or gaseous stream. Membrane filtration extends this application further to include the separation of dissolved solutes in liquid streams and for the separation of gas mixtures (Cheryan, 1998).

A membrane is a selective barrier which permits passage of certain components and retain certain other components of a mixture (Cheryan, 1998). A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure; it may be solid or liquid; it may be neutral, may carry positive or negative charges, or may be bipolar (Porter, 1990). The most important membrane used today in separation processes is composed of a rather sophisticated asymmetric structure. An asymmetric membrane consists of a very thin (0.1 to 1 μm) selective skin layer (active layer) on a highly porous (100 to 200 μm) thick substructure (support layer) (Porter, 1990). Asymmetric membranes are widely used in pressure driven membrane processes due to the unique properties in terms of high mass transfer rates and good mechanical stability (Porter, 1990). Depending on the dimensions of the dissolved substance different radii of pores can be adopted for the membranes (Cheryan, 1998). If a "true" solution is subject to purification or concentration, for example desalination of sea water, reverse osmosis (RO) (1-10 Å) and nanofiltration (NF) (10 Å) processes are used (Rushton et al., 1996; Cheryan, 1998). In case of the separation of bacteria, virus or substance with a high-molecular weight, ultrafiltration membranes are used, the significant dimension of pores are 10 – 200 Å (0.001-0.02 μm) and the process is known as ultrafiltration (UF) (Rushton et al., 1996; Cheryan, 1998). Finally, if it is necessary to separate colloidal particles, as in case of purification of wine and beer, filtration of particles in the size range 200-10^5 Å (0.1-10 μm), using relatively open membranes is described as microfiltration (MF) (Rushton et al., 1996).
The essence of the membrane separation process can be described as the following. A feed aqueous solution contains a dissolved component, which should be separated from the liquid phase. In the case of demineralization, reverse osmosis and nanofiltration, the dissolved salt must be retained by the membrane, as a result purified water is obtained behind the membrane in the permeate solution (Hwang and Kammermeyer, 1981). In the case of concentration, the purpose is to find a concentrate (obtained in the feed solution), which will then undergo further process (Hwang and Kammermeyer, 1981). Hence membranes are capable of solving simultaneously both problems: demineralization and/or concentration.

In RO and NF processes, the pumping system has to overcome the osmotic pressure of the salt in water. This leads to the necessity for large pressure drops (25-70 bar) across the membranes in order to achieve acceptable filtrate rates (Rushton et al., 1996). In contrast, UF and MF processes operate at relatively low pressures (0.07-7 bar) (Rushton et al., 1996).

Therefore, in the case of NF or RO the following requirements are needed:

I. high transmembrane pressure should be used;

II. almost the whole volume of the feed solution should be pushed through the membrane.

Both result in high running costs.

In this thesis the emphasis has been on studying the separation efficiency of Ultrafiltration processes. The aim of this thesis is to use Ultrafiltration (that is at a much lower transmembrane pressure) instead of NF or RO, therefore only a small portion of the solution should be pushed through the membrane, because concentration of solute in the permeate is substantially higher than in the feed solution.

The use of a polyelectrolyte in the feed solution is due to the considerations that ions such as potassium and chloride pass easily through the UF membrane, this would lead to the reduction of the concentration of chloride in the retentate side of the membrane, however the dissociation of the polyelectrolyte compensates this reduction, at the same time this increased presence of chloride ions, that can also cross the membrane, would originate an electric negative charge in the permeate side of the membrane. In order to keep the electroneutrality some positively charged ion must
pass through the membrane along with the newly dissociated chloride ions, as the polyelectrolyte ions are much bigger than the other cations present in the solution, potassium or similar ions are forced to cross the membrane. The overall process leads to a concentration of cations in the permeate that can be higher than in the feed solution.

This Thesis consists of six Chapters. After a brief introduction in Chapter I containing an overview of the project, Chapter II is focused on the literature review starting with description of membrane separation processes mainly nanofiltration and ultrafiltration. After this, a new method of an inorganic salt concentration using a polyelectrolyte in the feed solution during ultrafiltration is introduced; the last section of the literature review deals with the problems associated with an high level of boron in the environment and gives a summary of the current methods of boron removal. The experimental procedures are presented in Chapter III. A theoretical approach of an inorganic salt concentration in the presence of a polyelectrolyte during ultrafiltration is developed in Chapter IV. Determinations of polyelectrolyte charges and diffusion coefficients of polyelectrolytes through conductivity measurements are proposed and a model is developed and validated in Chapter V. Also in this chapter model parameters such as \(a\), \(b\) and \(g\) have been determined independently. Chapter VI contains the experimental results of ultrafiltration of different inorganic salts (\(KCl\), \(CsCl\) and others) in the presence of the cationic polyelectrolyte and boron ions in the presence of the anionic polyelectrolyte. The summary of this thesis conclusions and suggestions for future work are in Chapter VII.
CHAPTER 2: LITERATURE REVIEW

2.1 Membrane separation processes

2.1.1 Introduction

The osmosis process is analysed in many textbooks (Hwang and Kammermeyer, 1981; Bryk and Tsapyuk, 1989; Porter, 1990; Cheryan, 1998) and can be described as the following: an ideal semi-permeable membrane (i.e., permeable to water and non-permeable to dissolved substance), dividing two reservoirs, one of which (reservoir 1) is initially filled with pure water, and the second (reservoir 2) is a solution with the concentration of the dissolved substance $c_0$. The presence of the dissolved substance leads to the appearance of osmotic pressure (Fridrikhsberg, 1984; Bryk and Tsapyuk, 1989), which reduces pressure in the reservoir 2 in comparison to the pressure in the reservoir 1. This pressure difference causes flow of water from reservoir 1 into reservoir 2, as a result of this pure water flow entering solution 2 its gradual dilution occurs and this process is called osmosis. But if an increase pressure is applied (for example, with the aid of the piston) in solution 2 at a value higher than the osmotic pressure, then, because of the semi-permeability of the membrane, pure water will begin to flow from solution 2 into the reservoir with pure water 1; consequently the concentration of the dissolved substance will begin to rise in the solution 2. The process indicated is reverse with respect to the process of osmosis and is, therefore, called reverse osmosis (RO).

2.1.2 Substance transfer in the nanofiltration and ultrafiltration processes.

Firstly, we examine the reverse osmosis separation of a solution, when a dissolved substance is in the form of neutral molecules. The transfer of molecules in the solution occurs as a result of two processes (Bryk and Tsapyuk, 1989):

(a) transfer with the flow of water, this process is known as convective transfer,

(b) transfer caused by heterogeneity distribution of the concentration of a dissolved substance (this process is known as diffusion).
It appears only when the heterogeneity of the concentration of a dissolved substance is present and it attempts to equalize concentration everywhere in the solution (Bryk and Tsapyuk, 1989). Consequently, the flow of the dissolved substance through the membrane $J$ (Fig. 2.1) can be written as a sum of convective and diffusion fluxes (Hwang and Kammermeyer, 1981).

$$J = v c(x) - D c'(x)$$

(2.1)

where $v$ is the filtration rate of the solution through the membrane, given by the pressure drop $\Delta p$ across the membrane, i.e., $v = K \Delta p$ (Darcy's law), where $K$ is the permeability of the membrane (corrected for fluid viscosity); $D$ is the diffusion coefficient of the dissolved substance in the volume, the superscript indicates derivative.

![Fig. 2.1 Schematic representation of nanofiltration or ultrafiltration process](image)

0 feed solution
1 concentration polarization zone of thickness $\delta$
2 active layer of the membrane of thickness $h$
3 permeate

An ideal semi-permeable membrane allows only water to pass through, real membranes do not exhibit an ideal behaviour, because the dissolved substance can partially penetrate through the membrane. The membrane selectively leads the
dissolved substance to penetrate through the membrane pores less than the water. Because of this during the filtration of the solution through the membrane the water predominantly penetrates through the membrane. The dissolved substance is accumulated in the immediate proximity of the membrane, this leads to the rise of the concentration of the dissolved substance near the surface of the membrane at values higher than in the volume of solution. This phenomenon is referred to as concentration polarization (Hwang and Kammermeyer, 1981; Porter, 1990). Diffusion attempts to equalise concentration, creating a flux from the membrane to the bulk solution decreasing the concentration of the dissolved substance at the membrane surface (Bryk and Tsapyuk, 1989). The higher the concentration of the dissolved substance near the membrane, the more penetration of the dissolved substance through the membrane, which is extremely undesirable (Bryk and Tsapyuk, 1989). In order to help diffusion to remove the dissolved substance from the surface of the membrane (zone 0, Fig. 2.1), intensive stirring of the solution is applied, as a result of which a layer is formed near the membrane surface, known as the boundary layer or concentration polarization layer (Porter, 1990). The thickness of the layer is marked as $\delta$. Zone 1 in Fig. 2.1 is the zone of the concentration polarization, where the concentration of the dissolved substance is higher than the concentration in the feed solution (Zone 0, Fig. 2.1). The more intensive mixing in zone 0, the smaller $\delta$ and the lower the surface concentration of the membrane, $c_m$, becomes and the better the condition for the retention of the dissolved molecules (Hwang and Kammermeyer, 1981).

2.1.3 Reasons for the retention the dissolved substance by NF / UF membranes.

Let us study a flat surface in the aqueous solution. Let the surface be such that the molecules of dissolved substance are repulsed from the surface, but water is not repulsed. This is called the negative adsorption of the dissolved substance. Let us assume, that the phenomenon of negative adsorption exists. Thus the concentration of the dissolved substance is lowered near the surface than in the volume of the solution, at the same time, diffusion attempts to equalize the concentration. As a result of these two opposite tendencies, repulsion and diffusion, the layer of the thickness $d$ appears, where the concentration of the dissolved substance is lowered as compared with the feed concentration, $c_0$. The characteristic value of $d$ is 10 Å or $10^{-7}$ cm (Lyklema,
Let us place two plates from the same material at a distance from each other $h$, where $h < d$, in this case the concentration in the clearance between the plates will be less than the feed concentration, $c_0$. The slot examined is the simplest model of the pore of RO or NF membrane (Fig. 2.2), and the explanation is the fundamental starting point for understanding of the essence of the process (Martynov et al., 1980; Dukhin et al., 1988; Starov and Churaev, 1993).

Let $\Phi$ be the average potential of the forces of negative adsorption in the clearance of width $h$ (or a radius of a pore in a more general case). We consider the potential expressed in $kT$ units, where $k$ is the Boltzmann constant, and $T$ is the absolute temperature in K, correspondingly. The potential $\Phi$ depends on a radius of a pore, its characteristic value varies from 2 to 10 in the pores of RO or NF membranes (Dukhin et al., 1988). At the equilibrium the "state" of the molecules of the dissolved substance in the volume of solution and in the pores should be equal. Application of equality of chemical potential for the molecules of the dissolved substance in the volume and in a pore gives (Starov and Churaev, 1993):

$$c_p = c_0 \exp(\Phi)$$

where $c_p$ is the concentration in the membrane pores.

Fig. 2.2 Schematic representation of a membrane pore.
The equation (2.2) is a Boltzmann distribution. The concentration of the dissolved substance is lower where the energy is higher.

The principle of local equilibrium is the basic law of thermodynamics of the irreversible processes. According to this principle equation (2.2) is fulfilled between the surface concentrations of the solution through the membrane (furthermore, this property has been directly proven by Hall et al. (1997a). Returning to the diagram of the process (Fig. 2.1), we conclude, that Eq. (2.2) in the case of flow takes the following form: \( c(0^+) = c(0^-) \exp(-\Phi) \). It can be written as \( \gamma = \exp(\Phi) \), then the last equation is

\[
c(0^+) = c(0^-)/\gamma
\]

(2.3)

where \( c(0^+) \) is the concentration on the membrane from the membrane side, \( c(0^-) \) is the concentration on the membrane from the volume side, \( \gamma \) is the distribution coefficient and is the fundamental characteristic of the RO or NF membrane (Hall et al., 1997a).

2.1.4 Model describing the transfer of the dissolved substance inside the membrane.

The flow inside the membrane is due to the combined effect of the flow of water and the diffusion (because of the uneven concentration inside the membrane). The processes occurring inside the membrane are different from the processes in the feed solution. To consider these two processes two phenomenological coefficients are introduced (Hall et al., 1997a):

1. \( \alpha \) is a coefficient, that considers the difference in the convective flow of the molecules of the dissolved substance from the rate of transfer of water in the membrane (\( \alpha \) should be more than one because the membrane tries to repulse the molecules of the dissolved substance)

2. \( D_m \) is the diffusion coefficient of the dissolved substance inside the membrane. Qualitative assessments (Hall et al., 1997a) showed that \( D_m \) must be less than the volumetric coefficient of diffusion \( D \).
The homogeneous model of the membrane is used below (Hall *et al.*, 1997a). In this case, equations are written so that the entire membrane is permeable to water and dissolved molecules. This approach is called the *interpenetrating continuers* (Fridrikhsberg, 1984) and it is a convenient mathematical method for describing the processes, for porous bodies. Therefore, the equation, describing the transfer of the dissolved substance inside the membrane is:

\[ J = \alpha \nu c(x) - D_m c'(x) \]  \hspace{1cm} (2.4)

where \( J \) is the unknown flow of the dissolved substance.

The desired concentration of the dissolved substance in the emerging solution (permeate) is shown as \( c_p \) (zone 3, Fig. 2.1). This can be expressed through the unknown flow \( J \). In time \( \Delta t \), the volume of water through the membrane can be given as \( \Delta V = \nu \Delta t \), where \( \nu \) is filtrate rate through the membrane, in the same time the mass of the dissolved substance transferred through the membrane will be \( \Delta M = J \Delta t \).

Concentration \( c_p = \frac{\Delta M}{\Delta V} = \frac{J \Delta t}{\nu \Delta t} = \frac{J}{\nu} \), that also is the unknown expression, so we will rewrite as:

\[ c_p = \frac{J}{\nu} \]  \hspace{1cm} (2.5)

The boundary condition on the second surface of the membrane at \( x = h \), is obtained from the same principle of local equilibrium, as used on the front surface of the membrane. Now, it can be written as:

\[ c(h-) = c_p \]  \hspace{1cm} (2.6)

**2.1.5 The rejection coefficient and its expression with an aid of the above theory.**

The fundamental characteristic of the membranes is the rejection coefficient \( R \) defined as (Porter, 1990):

\[ R = 1 - \frac{c_p}{c_0} \]  \hspace{1cm} (2.7)
If the dissolved substance does not penetrate the membrane, then \( c_p = 0 \) and \( R = 1 \), which is most desirable in reverse osmosis. But if the membrane does not retain any of the dissolved substance, then \( c_p = c_0 \) and \( R = 0 \) and this membrane is not fit for the purpose. The case \( R = 1 \) is not achievable in practice, but it is possible to get very close (Bryk and Tsapyuk, 1989).

Solving differential first order equations (2.1) and (2.4) with the boundary conditions \( c(-\delta) = c_0 \) and also with (2.3), (2.5) and (2.6), we find an expression for the unknown concentration of the permeate solution and from formula (2.7) obtain rejection coefficient (Hall et al., 1997a):

\[
R = 1 - \frac{1}{1 + \left( \frac{\gamma}{\alpha} - 1 \right) \exp(-\nu\delta/D)(1 - \exp(-\alpha h/D_m))}
\]  

(2.8)

The qualitative form of dependence \( R(\nu) \) shows that there is an optimum rate of filtration of the solution through the membrane \( \nu_{opt} \) (and, consequently, the optimum corresponding pressure drop \( \Delta p_{opt} \)), when rejection coefficient is maximum. This conclusion is in accordance with the experimental results (Hall et al., 1997b).

2.1.6 Charged membranes and the nano- and ultra- filtration separation of electrolyte solutions.

The theory of RO/NF separation presented above is not always applicable to solutions of electrolytes (Starov and Churaev 1993). However, in practice it works satisfactorily, although the basic coefficient of theory, the rejection coefficient strongly depends on concentration, which is not considered in the theory. The modification of the theory is shown by Hall et al. (1997a).

Basic differences in the RO/NF separation of the solutions of electrolytes from the case examined above are as following (Starov and Churaev 1993; Hall et al., 1997a):

1. the spontaneous appearance of the electric field, which strongly influences the flow process;
2. the influence of its own charge of the membrane.

2.1.7 Spontaneous appearance of the electric field.

There are several examples of the existence of the electric field, for instance, in the case of the binary solution of electrolyte (a solution \( A^+ + B^- \)). Let us assume that cations \( A^+ \) are not very mobile (their diffusion coefficient is very small) and large enough so that they can hardly penetrate the pores of the membrane, and anions \( B^- \), on the contrary, are more mobile and small to easily go through the membrane. If the electric field did not appear, that would create the separation of charges on both sides of the membrane, which is practically impossible. As a result an electric field appears, which equalizes the concentrations of cations and anions and makes the solution electrically neutral (Hall et al., 1997a).

2.1.8 Influence of its own charge of the membrane.

In the aqueous solutions the pores of the majority of nanofiltration membranes bear a charge (for example, acetate cellulose membranes). The simplest mechanism of its formation is the following (Fridrikhsberg, 1984). On the surface of pores are groups of the type \( R-OH \), which dissociate in aqueous solutions, returning the cation of hydrogen into solution \( R-O^- + H^+ \). The appearing charge within the framework of the homogeneous model is characterized by the space charge of an entire membrane \( \rho \), as a whole, which strongly depends on pH of the solution and its concentration (Hall et al., 1997b). It is obvious, that there is an influence of the charge of the membrane on the process of separation and transferring the ions. Assuming that the membrane has a strong negative charge. In this case there are a lot of cations in the membrane and they tend to balance the volume charge of the membrane to make it electro-neutral. These cations practically can not leave the membrane. In view of the presence of the distribution of Boltzmann (Fridrikhsberg, 1984), the small surplus of anions (and an equal quantity of cations, for observing the condition of electroneutrality) is present nevertheless inside the membrane. Specifically, this small surplus can be transferred through the membrane.
The important consequence of the developed theory (Gorskii et al., 1988; Hall et al., 1997a) is the presence of the relation $\rho/c_0$, where $\rho$ is the volume charge of the membrane. Consequently, the higher the concentration of electrolyte in the feed solution is, the less influence of the charge of the membrane on the process of separation, and the worse the process of separation. This is very well confirmed by the experiments (Hall et al., 1997b).

The simplest situation described here is complicated in the case of the presence in the feed solution of the mixture of different electrolytes (Fridrikhsberg, 1984) (multicomponent solution). With the appearing of the electric field, the charge of the membranes becomes a complex function not only of the general concentration of electrolyte, but also of which electrolytes and in what proportion they are present in the feed solution. Of all possible special features of processes let us note only one which gives the possibility of concentration of one of the electrolytes of a mixture in the permeate solution. The mixture of two electrolytes in the feed solution is made of electrolyte 1 and electrolyte 2. If the concentration of electrolyte 1 is much more than the concentration of electrolyte 2, then, the electric field will be in essence created by electrolyte 1, and electrolyte 2 will be transferred through the membrane in this field, practically without influencing it. There are possibly two directly opposite situations:

1. the electric field impedes the passage of electrolyte 2
2. the electric field accelerates the passage of electrolyte 2

In the case (b) electrolyte 2 is concentrated in the permeate despite the fact that electrolyte 2 without the presence of electrolyte 1 can be rejected by the membrane (Bryk and Tsapyuk, 1989). This example demonstrates the importance of the electro-kinetic phenomena of proceeding in the processes of reverse osmosis.

The ideas about the nanofiltration separation of solutions presented make it possible to forecast and to calculate the processes indicated. The theory is based on well-known physical concepts.
2.2 Concentration of inorganic salts in the presence of a polyelectrolyte during Nanofiltration or Ultrafiltration

The phenomenon of salt concentration in the filtrate (Gorskii et al., 1988) is further investigated in this work. An analysis of the literature available on this subject showed that similar effects for reverse osmosis were firstly reported in 1974 by Lonsdale and Push and later by Hall et al. (1997b). In subsequent papers, the process was mathematically modelled on the basis of the Nernst-Planck equations for ion fluxes with the use of some phenomenological parameters (Lonsdale and Push, 1974; Migalatii et al., 1987; Perry and Linder, 1989; Spiegler and Kedem, 1966; Starov and Churaev, 1993).

In this work the mathematical elucidation of the effect is based on a description of the salt concentration on both sides of the membrane, determined by the Donnan equilibrium and the process is shown to be effective with ultra- and nanofiltration membranes.

Other factors influence the rejection ability of membranes with respect to various components (Starov et al., 1991; Vonk and Smith, 1983a; Vonk and Smith, 1983b), whereby the flow of an electrically neutral solution through a porous solid matrix gives rise to an electric potential accelerating the motion of one ionic species while retarding the others. Bryk and Tsapyuk (1989) states that electrostatic forces mediate a component occurring in solution in the dissociated state. This was substantiated by examples showing the effect of charges of solution components on the rejection of a low-molecular-weight electrolyte. This influence can be also explained by the Donnan effect (Vonk and Smith, 1983a). Perry and Linder (1989) interpreted a negative salt rejection in terms of the theory of reverse osmosis, developed by Spiegler and Kedem (1966), with allowance for the Donnan exclusion correction in the driving force component responsible for the salt transport.
In the present study the basis of the previous theory (Vonk and Smith, 1984) is developed providing a mathematical model describing the transfer of a low-molecular-weight electrolyte through an ultrafiltration membrane in the presence of a polyelectrolyte, which is completely rejected by that membrane.

Considering the nanofiltration or ultrafiltration of an inorganic salt, $\text{KCl}$, which is assumed to be a strong electrolyte and a water soluble polyelectrolyte in the feed solution. The membrane is assumed completely impermeable to the polyelectrolyte molecules. The salt completely dissociates according to $\text{KCl} \rightarrow \text{K}^+ + \text{Cl}^-$.

Concentrations of the salt and water soluble polymer in the feed solution are $c_0^+$ and $c_0^-$ respectively. Schematic representation of the process is given in Fig. 2.1.

The process can be rationalised as follows (Prokopovich et al., 2005):

1) During ultrafiltration potassium and chloride ions pass through the membrane

2) As the chloride concentration reduces the polymer chloride will dissociate to release more chloride ions.

3) The polymer cations are rejected by the membrane, but chloride ions passing through the membrane, originating from the polymer chloride complex, which will be accompanied by potassium ions, in order to maintain electroneutrality; thus concentrating the potassium ions within the permeate.

The above scheme provides a simple mechanism by which the potassium will concentrate in the permeate and, in practice, all three of the above steps will occur simultaneously.
2.3 Boron characteristics and removal

2.3.1 Introduction

The element boron, chemical symbol B and atomic number 5, has two stable isotopes of mass 10 and 11, the latter being more prevalent at 81.17%, therefore the FW is 10.85 (Muetterties, 1967).

Boron is a fairly abundant element, its content in the lithosphere is about $10^{-3}$ weight percent (Nemodruk and Karalova, 1965). The elemental form of boron is unstable in nature, boron is found combined with oxygen in a wide variety of hydrates alkali and alkaline earth-borate salts and borosilicates. Boric acid, derived from weathered rocks or volcanic activity, is eventually incorporated into marine sediments (Nemodruk and Karalova, 1965).

Boron is a necessary trace nutrient for plants; it is apparent that boron is essential for the normal growth and functioning of apical meristems (Nemodruk and Karalova, 1965).

The formation of the hydroborate ion on ionization of boric acid is spontaneous (Muetterties, 1967):

$$B(OH)_3 + 2 H_2O \leftrightarrow B(OH)_4^- + H_3O^+$$

Boron may occur naturally in some water or its presence may originate from industrial waste discharges or agricultural use of boron pesticides or fertilizers. Its concentration should not exceed 10 mg/l in wastewater (Muetterties, 1967).
2.3.2 Boron uses

Boron compounds are widely employed, for example (Nemodruk and Karalova, 1965):

- in medicine for the preparation of disinfectants and drugs;
- in neutron-absorbing materials, e.g. for control rods and neutron shields; due to this reaction:

\[ ^{10}B + ^{1}n \rightarrow ^{7}Li + ^{4}He + 2.5\text{MeV} \]

- nuclear properties of boron-10 have found applications in research into treatment of brain tumours;
- in the glass industry for the production of optic and chemically stable glass;
- as components of enamels to increase hardness;
- to protect metal against oxidation during soldering;
- as additive to electrolytes in nickel plating;
- in the cosmetic, leather, textile, rubber and paint industries;
- in the wood-processing industry as a protection against molds.

The introduction of small amounts of boron or its compounds into the soil considerably increases the harvest of many plants including sugar beet, root crops for animal feeding, corn, flax, cotton and tobacco (Nemodruk and Karalova, 1965).

In recent years the production of boron and its compounds has greatly increased. The increased use of boron in flame-retardants may have an effect on surface water concentration, this is relevant where boron concentration are high, around 500 µg/l. This, coupled with the proposed World Health Organisation (1998) limit of 300 µg/l, and the inability of reverse osmosis to remove more than 50/70 % point to a problem with boron.
2.3.3 Boron in aqueous solutions

In general, two boric acid types exist in the free state, metaboric HBO₂ and orthoboric B(OH)₃. Each type may be converted to the other by either hydration or dehydration at certain conditions. In solution, metaboric acid converts rapidly to orthoboric acid due to hydration (Muetterties, 1967; Lou et al., 1999).

Boric acid in solution dissociates weakly \((k_1=7.3\times10^{-10})\) to form monoborates and some polyborates, depending on temperature, pH and concentration. (Muetterties, 1967; Lou et al., 1999). At a lower pH than 7, boron is present in its non dissociated form and at a pH greater than 11.5, it is present in the dissociated borate form (Kano and Darbouret, 1999). The primary species at the acidic and basic extremes are \(B(OH)_3\) and \(B(OH)\)⁻, respectively (Muetterties, 1967; Lou et al., 1999). At low concentration \(B(OH)\)⁻ (< 0.025 M as boron) is the only significant species in solution, while at higher concentration polyborates: tri-, tetra- and penta-borates may exist (Lou et al., 1999):

\[
\begin{align*}
B(OH)_3 + 2H_2O & \leftrightarrow [B(OH)_4]^- + H_3O^+ \\
2B(OH)_3 + [B(OH)_4]^+ & \leftrightarrow [B_3O_3(OH)_4]^+ + 3H_2O \\
2B(OH)_3 + 2[B(OH)_4]^+ & \leftrightarrow [B_4O_5(OH)_5]^+ + 5H_2O \\
4B(OH)_3 + [B(OH)_4]^+ & \leftrightarrow [B_5O_6(OH)_4]^+ + 6H_2O
\end{align*}
\]

Boron, whose electronic configuration is 1s² 2s² 2p, has 3 valence electrons and forms planar, tricovalent derivatives that are electron deficient, which, similarly to Lewis acids, accept 2 electrons from bases to complete the boron outer-shell octet and give tetrahedral adducts. Boric acid exemplifies this behavior by ionizing, in aqueous solution, not by direct deprotonation, but by hydration and subsequent ionization, to give the symmetrical borate anion (Kano and Darbouret, 1999).
2.3.4 Toxicity of Boron

Everyone is exposed regularly to small amounts of boron; generally this amount is not harmful because boron is regularly excreted in faeces and urine (WHO, 1998). Excretion is relatively rapid, occurring over a period of few, or possibly several, days. If food or drinking water contains abnormal amounts of boron, people can be exposed to excesses of this compound (WHO, 1998).

Short and long term oral exposures to boric acid or borax by laboratory animals have demonstrated that male reproductive tract is a consistent target of toxicity. Testicular lesions have been observed in rats, mice and dogs exposed to boric acid or borax. Other symptoms that have been linked to long-term exposure to boron include loss of appetite, vomiting, diarrhoea, loss of hair, skin rashes, anaemia and convulsions (WHO, 1998).

Negative results in a large number of mutagenicity assays indicate that boric acid and borax are not genotoxic (WHO, 1998). In long-term studies in mice and rats, boric acid and borax caused no increase in tumour incidence (WHO, 1998).
2.3.5 Boron determination

For the determination of Boron several methods can be used, the main groups of these are (Nemodruk and Karalova, 1965):

- gravimetric analysis
- titrations
- photometry

The first group involves the transformation of Boron in Calcium or Magnesium borate, drying the solution an evaluating the mass of borate (Nemodruk and Karalova, 1965).

The direct titration of Boric acid with alkali is not possible since boric acid is very weakly dissociated so the equivalent point is approximately at pH = 11. It is very difficult to find an indicator which gives a sharp colour change in this pH region (Nemodruk and Karalova, 1965).

Titrimetric methods are based on the capability of boric acid to form, with polyhydric alcohols or sugars, complexes which exhibit stronger acid properties and can therefore be titrated with alkalis. For this purpose mannitol or glycerol are usually employed (Nemodruk and Karalova, 1965).

Photometric methods are especially suitable for the determination of micro-amounts of Boron. Since Boron has no chromophoric properties, only coloured reagents can be used for its photometric determination (Nemodruk and Karalova, 1965).
The reagents used for this purpose exhibit the presence of particular groups, for example:

![chemical structures](image)

Groups like (a) are present in Curcium, while groups like (b) are present in Azo-compounds (Azomethine-H); these are obtained by coupling diazotized H-acid (1-amino-2-naphto-3,6-disulfonic acid) with resorcinol (Nemodruk and Karalova, 1965).

For water analysis, if the concentration of Boron is below 0.5 ppm., the best determination is photometric; if the concentration is higher titration methods are more convenient (Nemodruk and Karalova, 1965).

A spectrometric method using azomethine-H is available for the determination of borate in water. The method is applicable to the determination of borate at concentrations between 0.01 and 1 mg/litre. The working range may be extended by dilution (ISO, 1990).

Nowadays a widely used method for the analysis of boron in bone, plasma, and food is inductively coupled plasma atomic emission spectroscopy (Hunt, 1989). This method is also used for water (ISO, 1996) and wastewater (Hunt, 1989). Detection limits in water range from 6 to 10 μg of boron per litre.
Inductively coupled plasma mass spectroscopy (ICP-MS) is a widely used nonspectrophotometric method for the analysis of boron, as it uses small volumes of sample, it is fast, and applies to a wide range of materials (fresh and saline water, sewage, wastewater, soils, plant samples, and biological materials). ICP-MS can detect boron down to 0.15 μg/litre (WHO, 1998). Using direct nebulization, ICP-MS can give a detection limit of 1 ng/g in human blood, human serum, orchard leaves, and total diet (Smith et al., 1991).

2.3.6 Boron removal

Boron is widely distributed in the environment, occurring naturally or from anthropogenic contamination, mainly under the form of boric acid or borate salts. Even if it is an important micronutrient for plants (Wilcox, 1960; Waggon, 1969), animals and humans, the range between deficiency and excess is narrow. The acceptable daily intake (Murray, 1996) is 0.3 mg boron kg⁻¹ day⁻¹, which is well above the normal exposure levels. World Health Organisation (WHO, 1998) has recommended a limit of 0.3 mg boron per litre for drinking water.

Most of the surface and ground water are below this limit, except in the vicinity of borate mines (Okay et al., 1985) or some industrial discharges (Recepoglu and Beker, 1991), where concentrations can reach up to 7 mg/l.

Seawater contains about 5 mg/l while some gaseous mineral waters contain a few mg/l (Song and Huang, 1987). Boron removal has given rise to numerous works (Pilipenko et al., 1990; Nicolaï et al., 1992). The main processes that have been studied are:

- Precipitation (Chang and Burbank, 1977; Badruk et al., 1999a; Itakura et al., 2005).

- Electrocoagulation (Yilmaz et al., 2005).
Solvent extraction (Egneus and Uppstrom, 1973; Brown and Sanderson, 1980; Ayers et al., 1981; Poslu and Dudney, 1983; Tsuboi et al., 1990; Nano et al., 1994; Matsumoto et al., 1997; Karakaplan et al., 2004).

Adsorption (Choi and Chen, 1979; Okay et al., 1985; Hayashi et al., 1991; Ooi et al., 1996).

Ion-exchange (Kunin and Preuss, 1964; Recepoğlu and Beker, 1991; Badruk et al., 1999a, b; Kabay et al., 2004 a, b; Ristic and Rajakovic, 1996).

Membrane processes such as: membrane filtration after complexation (Smith et al., 1995), RO (Magara et al., 1998; Pastor et al., 2001; Prats et al., 2000; Dey et al., 2001; Qin et al., 2002; Qin et al., 2005) and electrodialysis (Melnik et al., 1999).

2.3.6.1 Precipitation

Chang and Burbank (1977) investigated removal of boron from incinerator water with high hydrous metallic oxides. They used ferrous sulphate, aluminium sulphate and sodium aluminate for precipitation and coagulation. Boron removal was 30.6% by ferrous sulphate, 86.7% by aluminium sulphate, 65.1% by sodium aluminate (Badruk, 1999a).

Itakura et al. (2005) developed a new hydrothermal treatment technique to recover boron from waste water as recyclable precipitate $Ca_2B_2O_5\cdot H_2O$ from aqueous solutions. As a result, they found that the hydrothermal treatment using calcium hydroxide as a mineralizer converted boron in the aqueous media effectively into calcium borate, $Ca_2B_2O_5\cdot H_2O$. In the optimal hydrothermal condition, more than 99% of boron was collected from the synthetic wastewater of 500 ppm. Thus, the hydrothermal treatment in the presence of calcium hydroxide was recommended as one of the most effective technique to recover boron from aqueous media (Itakura et al., 2005).
2.3.6.2 Electrocoagulation

Boron removal from wastewaters by electrocoagulation using aluminium electrode material was studied in (Yilmaz et al., 2005). Several working parameters, such as pH, current density, boron concentration, type and concentration of supporting electrolyte were studied in an attempt to achieve a higher removal capacity. The use of aluminium electrode material in the treatment of boron wastewater by electrocoagulation was found to be pH dependent. The most effective removal capacity was achieved at the pH 8. Although energy consumption increased with decreasing boron concentration, when the conductivity of these solutions were low, boron removal efficiency was higher at 100 mg/l than that of 1000 mg/l. Current density was an important parameter affecting removal efficiency. Boron removal efficiency and energy consumption increased with increasing current density from 1.2 to 6.0 mA/cm².

2.3.6.3 Solvent extraction

Boron exists as boric acid or borate in an aqueous solution. According to Brown and Sanderson (1980), extractants for boron are classified into three groups:

a) Extract ion of boric acid without any reactions (physical extraction)

b) Extract ion of boric acid with a reaction which forms of a neutral ester

c) Extract ion of boric acid with a reaction with tetrahydroxyl borate to form a borate salt complex.

In the case of physical extraction, high extractability is not attainable. The extractants belonging to groups (b) and (c) are suitable for extracting boron from acidic and alkaline solutions (Brown and Sanderson, 1980; Matsumoto et al., 1997), respectively.

Among aliphatic 1,3-diols belonging to group (b), it was reported that 1,3-diols with 8 or 9 carbon atoms (Egneus and Uppstrom, 1973; Matsumoto et al., 1997) have a maximum extraction capacity. 2-ethyl-1,3-hexanediol (EHD) was therefore used for the recovery of boron from the coal fly ash (Matsumoto et al., 1997) and geothermal water.
Nano et al., 1994; Matsumoto et al., 1997). Later, Karakaplan et al. (2004) studied the extraction ability of 2,2,5-trimethyl-1,3-hexanediol. They showed that extraction efficiency increased with increasing concentration of 2,2,5-trimethyl-1,3-hexanediol and the best extraction of boron (96.8%) was found to be at equilibrium pH of 2 with 0.5 M of 2,2,5-trimethyl-1,3-hexanediol.

Chloroform, toluene, chlorobenzene, 2-octanol and n-amyl alcohol were found to be suitable solvents for the solvent extraction of boron. The boron complex can be recovered from the organic phase by treatment with an aqueous solution of sodium hydroxide. The highest ratio (96.7%) of boron was recovered by 0.1 M of sodium hydroxide solution.

However, because the solubility of EHD in an aqueous solution is high (Brown and Sanderson, 1980; Matsumoto et al., 1997), the recovery of boron from wastewater using EHD is practically impossible. In the literature an extraction system for boric acid using 2-buthyl-2-ethyl-1,3-propanediol (BEPD) was reported (Matsumoto et al., 1997). It was expected that the solubility of BEPD in an aqueous solution would be lower than that of EHD because of the increase in the carbon number from 8 to 9 (Matsumoto et al., 1997).

Other researches (Ayers et al., 1981; Poslu and Dudeney, 1983) proposed to use a mixture of EHD and 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylol-phenol (CTMP). They found that mixed reagents in a 1:1 concentration ratio gave an enhanced extraction in the pH range 8-12 and extraction became essentially pH independent when the EHD/CTMP ratio was 3:1.

A combined process of adsorption and solvent extraction techniques has become attractive as a recovery process for boron because it can treat and purify large quantities of wastewater easily (Tsuboi et al., 1990; Matsumoto et al., 1997).
2.3.6.4 Adsorption

Adsorption of boron has been extensively studied on different oxides such as active carbon (Choi and Chen, 1979; Ooi et al., 1996), magnesium oxides (Okay et al., 1985), hydrous cerium oxide (Hayashi et al., 1991).

Choi and Chen (1979) offered the adsorption method for the removal of low levels of boron from solution. Three types of adsorbents were evaluated for the boron adsorption study: activated carbon (Filtrasorb®); activated bauxite; and activated alumina. The authors examined dependence of boron removal from the following parameters: the boron concentration in the solution, pH, duration of treatment (contact time), salinity, and competition with or interference by other chemical species and they finally concluded that boron removal efficiency generally increases with decreasing initial concentration of boron in the solution. Filtrasorb® showed a more pronounced initial concentration effect than the other adsorbents. Regardless of the characteristics of the background solution, a boron removal efficiency of about 90% can be achieved with Filtrasorb® (with an adsorbent dosage of 25 g/l) if the initial concentration of boron in the solution does not exceed 5 mg/l. The removal efficiencies of boron by activated bauxite and activated alumina (with an adsorbent dosage of 25 g/l) are less than 70% at the same initial concentration of boron. The optimum pH for boron removal under experimental conditions depends on both the characteristics of the background solution and the type of adsorbent. The optimum pH shifts to more alkaline pH when the solution salinity increases. However, salinity effects on both optimum pH and on removal efficiency are found only up to a certain limit of salinity for a given adsorbent. At above this value no additional effect on the removal efficiency was seen. The removal efficiency decreases sharply with increasing salinity up to about 0.8 % for Hydro Darco®, 0.5 % for Filtrasorb®, 0.8 % for activated bauxite, and 1.0 % for activated alumina. Generally, the presence of chemical species such as calcium, magnesium, silica, and sulphate results in a reduction in boron removal efficiency. However, the effects increase only up to certain limits, and no additional effect was seen.
2.3.6.5 Ion exchange

In the case of ion exchange processes, the weak dissociation of boron salts would require the use of a strong basic ion exchanger causing all anions of the solution to be retained, resulting in a very high regeneration cost (Itakura et al., 2005). A boron-specific ion exchanger is therefore the only solution for achieving economic boron removal (Recepoglu and Beker, 1991) through this kind of process.

According to the procedure proposed by Kunin and Preuss (1964) an ion exchange resin that is specific for boron can be prepared by the reaction of the chloromethylated copolymer of styrene and divinyl-benzene with N-methyl-glucamine. The product, although a weak base anion exchange resin, exhibits specificity for boron analogous to that of polyhydric alcohols such as mannitol, and a high capacity for boric acid over a wide range of conditions (Kunin and Preuss, 1964).

Studies employing columns being demonstrated by Badruk et al. (1999a, b) and Kabay et al. (2004 a, b), boron removal from wastewaters of geothermal plant was studied using N-glucamine type of resin so-called Diaion CRB 01, Diaion CRB 02 and Purolite S 108.

Ristic and Rajakovic (1996) studied the separation of boron compounds, boric acid and borax, with anion-exchange resins, before and after impregnation with citric acid and tartaric acids. They proposed that the presence of citric or tartaric acid was essential for the enhancement of the sorption capacity above that observed for the untreated resins. Sorption data showed that citric acid was a more effective impregnant than tartaric acid.

2.3.6.6 Boron removal using Membrane processes

2.3.6.6.1 Membrane filtration after complexation

Smith et al. (1995) offered a method of boron removal by polymer-assisted ultrafiltration. This boron removal technique exploited the pH-dependent complexation
between boric acid and a macromolecule containing vicinal diol groups in order to prevent boric acid from passing through the ultrafiltration membrane. The concentration of boron in treated waters was reduced from 10.5 ppm to less than 2 ppm through ultrafiltration of an aqueous solution containing boric acid and a polymer synthesized by N-methyl-D-glucamine (NMG) onto poly(epichlohydrin). It was shown (Smith et al., 1995) that NMG groups exhibited stronger affinity for boron than expected from equilibrium between NMG and boric acid. Problems with application of this technology include selection of sufficiently high molecular weight polymer fractions, development of polarization layers in dead-end filtration and precipitation of polymer under some industrially relevant saline conditions.

2.3.6.6.2 Boron removal by electrodialysis

In underground waters with low and medium salt content, the boron concentration can reach values as high as 40 mg/l (Melnik et al., 1999). Conventional electrodialysis was found to be only capable to remove about 42-75% of boron (Melnik et al., 1999). The effectiveness of boron removal by electrodialysis was shown to be dependent upon the type of the membrane, pH of the solution, degree of desalination, boron concentration in the feed and the presence of ion exchange resin in the desalting chamber. With optimum conditions, the boron concentration in the dialyzate cannot be reduced to 0.3-0.5 mg/l when the feed boron concentration in water is in excess of 4.5 mg/l. At boron concentrations of 4.5 and higher, it is necessary to use an additional conditioning of the dialyzate by boron-selective sorbents (Melnik et al., 1999).

2.3.6.6.3 Boron removal by reverse osmosis

Magara et al. (1998) developed a multi-stage RO membrane system for boron reduction in the production of drinking water from seawater desalination. They applied a low pressure (0.6-1.3 MPa) RO membrane at the second and third stage of the process. Their results showed that boron rejection enhanced with increasing operating pressure and remarkably increased with increasing feed pH in the range of 9-11 due to the conversion of boric acid to borate. However, they found that the boron rejection did not depend on its concentration in the raw feed water. In this way, it is possible to
eliminate the problem of deposition of salts on the membrane when increasing the pH of the water feed (Magara et al., 1998; Prats et al., 2000). However, an extra cost in terms of capital investment and chemical consumption would be involved in the additional stage (Magara et al., 1998; Pastor et al., 2001; Dey et al., 2001).

Prats et al. (2000) investigated the effect of feed pH and pressure on the removal of boron with different types of RO membranes in the desalination of brackish water. They found that boron rejection approached 100% when the pH was over 10.5 due to the negative charge of $H_2BO_3^-$, while the boron rejection was 40-60% not sensitive to pH in the range of 5.5-9.5. They also found that the boron rejection increased with an increase in the operating pressure.

Later Pastor et al. (2001) focused on boron removal using a RO plant with a second stage where pH of the RO permeate from the first stage was increased to 9.5. Their experimental results showed that boron rejection was almost 100% at pH around 9.5, and the economic evaluation indicated that an extra cost of 0.06 euros/m³ was involved for the second stage.

Dey et al. (2001) studied the effect of feed pH at the second stage on contaminant removal using a double-pass RO where permeate of the first stage RO was used as feed for the second stage RO in ultra-pure water production. Their results indicated that boron rejection increased significantly with an increase in feed pH in the range of 7.5 to 10.5.

The experimental results (Qin et al., 2002) from a feasibility study on the treatment and recycling of wastewater from metal plating using RO showed that the rejection for boron increased from 47 to 67% while operating pressure increased from 75 to 300 psi. The objective of the study (Qin et al., 2005) was to distinguish the factor contributing to the enhanced boron rejection in the reclamation of spent rinse water. The focus was on the effects of different known components used in the feed on boron
removal in laboratory tests. Boron rejection in a RO process is typically in the range of 40-60%. The results indicated that glycolic acid and antifoulants could not individually enhance boron rejection in a RO process. A high boron rejection of 95% was achieved as the concentration of iron in the feed was 10 times higher than that of boron, which might be due to formation of a complex between iron oxide and boron.

2.3.7 Conclusions

Some removal methods have been already proposed. Despite all the efforts dedicated to the boron removal problem, the ideal solution has still not been found and the existent methods have some disadvantages.

Co-precipitation method using metal hydroxide is an inefficient and environmentally ineffective process due to the important reasons: the removal rate is low; a large amount of metal hydroxide is required and large amount of unrecyclable wastes are discharged (Itakura et al., 2005). Evaporation–crystallization process is effective only in the streams with very high boron concentrations: more than several thousand ppm. In a solvent extraction processes, some expensive extractants should be used. Removal of boron from water by this process is easy, but most of the extractants are toxic (Hoşgören et al., 1997; Kahraman, 1995). The ion exchange method is rather effective in removing boron compounds from wastewater containing several hundred to thousand ppm of boron. However, the regeneration process of the selective ion exchange resins is required so frequently that only small amounts of wastewater can be treated (Badruk et al., 1999 a, b). In the case of RO to achieve relatively high elimination of boron it is necessary to apply a high working pressure, which requires high cost for manufacturing and maintenance (Itakura et al., 2005). Therefore, it is desired to establish an environmentally friendly removal/recovery method of boron from wastewater at lower cost and higher efficiency.
CHAPTER 3: MATERIALS AND METHODS

3.1 Dead-end filtration apparatus

All experiments were carried out in a dead-end stirred Amicon filtration cell. It had a capacity of 350 ml and could hold a disk of 6.8 cm in diameter. The maximum operating pressure of the cell was 4 bar. The stirrer was operated at a rate of 500 rpm which was maintained constant throughout the experiments. The individual components of the stirred cell are shown in Fig. 3.3. In this work the experimental set-up (Fig. 3.2) for a dead-end ultrafiltration was designed according to a typical stirred cell system (Fig. 3.1).

The set-up for the dead-end filtration is shown below (Fig. 3.1, Fig. 3.2). The typical dead-end stirred cell showing its individual components is presented at Fig. 3.3.

![Diagram](image_url)

*Fig. 3.1 Schematic of the experimental set-up for the use of a dead-end stirred cell*
1. pressure gauge;
2. pressure release valve;
3. three-way valve;
4. reservoir for feed;
5. stirred cell;
6. membrane;
7. stirrer bar;
8. gas (air) cylinder;
9. water bath;
10. magnetic stirrer;
11. permeate;
12. air filter

Compressed air at a measured pressure using the pressure gauge, acted as the driving force for the deadend filtration process. 350ml of a feed solution which contained various known concentrations of polymer solution and potassium chloride solution were filtered. The metal ion concentrations in the feed and filtrate solutions, collected with the measuring cylinder, were analysed using AAS.
Fig. 3.2 The experimental set-up for the dead-end ultrafiltration
Fig. 3.3 Schematic of a typical dead-end stirred cell showing its individual components

1. Pressure Inlet;
2. Pressure Relief Valve;
3. Transparent Body;
4. Stirring Bar;
5. O-Ring;
6. Membrane;
7. Membrane Support;
8. Filtrate Outlet;
9. Beaker Design;
10. Wrap-Around Clamp;
The cellulose acetate membranes UFM-50, UFM-100 and UFM-200 were used in the filtration experiments. The membranes were synthesized at Polimersintez Research Corporation, Vladimir, Russia. The effective area of a membrane was 0.4534 cm². The membranes were immersed for 24 hours in ultra pure water before being used.

In all filtration experiments, the membranes were firstly pressurised in order to stabilise their performance. Wetting the membranes by pressurisation prior to filtration is important for ensuring maximum selectivity and flux. The pressure used in stabilisation was between 0.5 and 4.0 bar. The stabilisation time used in the experiments varied between 15-25 minutes.

After the stabilisation was finished, the ultra pure water flux at a set of pressures (0.5 - 4.0 bars) was measured. The flux was measured after 15 minutes of filtration. The pre-treatment was performed until a linear dependence of the filtration rate on the pressure drop across the membrane was obtained.

When the ultra pure water flux had been obtained, the filtration experiment could be started. The operating pressures were in the range of 0.5 - 4.0 bars. Filtered compressed air was used in the filter cell to provide the pressure for filtration. The gathering of the permeate samples was started after 5-10 minutes of filtration. The permeate was collected for 10-30 minutes, depending on the permeate flux. About 15-20 ml of permeate was collected from each filtration procedure. The flux volume was measured at a fixed time. The flux was then calculated from the time of permeate collection and the membrane area of the module.

Filtration experiments were carried out with ultra pure water, different concentrations of inorganic salts solutions and mixtures of different concentrations of salts with different concentration of the polyelectrolyte solutions. The experiments were made at temperature 20±2 °C.
The filtration experiments were finished by measuring the water flux in order to see whether was any change in the membrane performance during the experiments, caused by e.g. irreversible fouling.

3.2 Filtration procedures

3.2.1 Filtration procedures for potassium and cesium concentration

The solutions running through the filtration apparatus, described above, were prepared with the following chemicals used as low-molecular-weight inorganic solutes: analytical grade $KCl$, $KNO_3$, $K_2SO_4$, CsCl and $MgCl_2$. A commercial synthetic water-soluble polymer poly(diallyl-dimethylammonium chloride) (PDDA, ZETAG™ 7125, CIBA SC (WT) Bradford, West Yorkshire, Great Britain) was used as a polyelectrolyte.

The stock solutions were prepared using 450 g/l PDDA solution and 0.1 mol/l inorganic salt solution. The metal ion content in the experiments, $c_+$, varied from $0.4 \times 10^{-3}$ mol/l to $3.0 \times 10^{-3}$ mol/l. The PDDA concentrations prepared were 0.05; 0.1; 0.2; 0.3; 0.4; 0.5; 0.8; 1.0; 2.5 g/l and 5.0 g/l. The corresponding molar polymer concentrations $c_0$ ranged from $3.6 \times 10^{-7}$ mol/l to $3.6 \times 10^{-5}$ mol/l.

The metal contents in solutions were determined by Atomic Absorption Spectrometer (AAS) (Varian Limited, Birchwood Science Park, Warrington, Cheshire, WA3 7BM, UK). The concentration of a polyelectrolyte in solution was determined by dry residue method with a drying temperature of 90 °C (oven, Salvis, Model C-G, Serial No 725, Exclusiveranges Ltd 1, Sutherland Court, Brownfields, Welwyn Garden City, Hertfordshire, AL7 1BJ, United Kingdom).

3.2.2 Filtration procedures for boron concentration

Cellulose acetate membranes UFM-100 with a pore size of 10 nm were used during filtration experiments. The membranes were pressurised for 20 minutes at 0.5-4.0 bar and the flux of ultra pure water was measured before and after filtration. Boron solutions were prepared using sodium borate and boric acid. The final boron concentrations in the working solutions used were in the range of 0.4-2.0 ppm. Pure boron solutions were filtered first, then an anionic polyelectrolyte was added to the boron solutions. The anionic polyelectrolyte used was: poly(sodium-4-styrenesulfonate) (NaPSS) with molecular weight 200 kDa (Aldrich, UK). The concentrations of the
polyelectrolyte in the feed solution varied between 0.5 and 5.0 g/l. In all experiments deionized water from a Milli-Q system was used.

3.3 Atomic Absorption Spectrometer (AAS)

The Varian SpectrAA atomic absorption spectrometer (AAS) shown in Fig. 3.4 was used to determine the concentration of the metal ions presented in both the feed and permeate solutions. The major components of the AAS are: light source, absorption cell, monochromator, detector and display.

A hollow cathode lamp that acts as a light source emits a light spectra specific to the type of element it is made of. The light source is focused through a sample cell into a monochromator. The light source is mechanically chopped to enable differentiation between the light from the source and the emission from the sample cell. The light is dispersed by the monochromator and the specific wavelength light isolated enters a photomultiplier tube detector. The amount of light attenuation in the sample cell is converted into sample concentration.

The working conditions used are summarized in the following Table 3.1.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Wavelength (nm)</th>
<th>slit width (nm)</th>
<th>optimum working range (µg/ml)</th>
<th>Lamp current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cesium</td>
<td>455.5</td>
<td>0.5</td>
<td>4-1200</td>
<td>20</td>
</tr>
<tr>
<td>potassium</td>
<td>769.9</td>
<td>1.0</td>
<td>1-6.0</td>
<td>5</td>
</tr>
<tr>
<td>magnesium</td>
<td>202.6</td>
<td>1.0</td>
<td>0.15-20</td>
<td>4</td>
</tr>
</tbody>
</table>

In addition the oxidizing agent was acetylene.
For each metal ion, prior sample analysis, a calibration curve was obtained using standard solutions. A typical calibration curve is shown in Fig. 3.5 which is for cesium determination.

Fig. 3.4 Varian SpectrAA atomic absorption spectrometer

Fig. 3.5 Cs calibration curve
3.4 Ion Exchange Chromatography

Anion concentrations ($\text{Cl}^-$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$) were analysed with ion-exchange chromatography (Dionex DX 1500) equipped with a column (IonPac® AS 11) using 21 mM sodium hydroxide as eluent, the picture of the apparatus is in Fig. 3.6. The chromatogram showing the separation of the analysed ions is shown in Fig. 3.7 and parameters of the chromatogram are presented in Table 3.2.
Fig. 3.7 Example of a chromatogram (1- $Cl^-$, 2- $SO_4^{2-}$, 3- $NO_3^-$)

Table 3.2 Essential parameters of the ion exchange chromatogram

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Retention time (min)</th>
<th>ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.98</td>
<td>$Cl^-$</td>
</tr>
<tr>
<td>2</td>
<td>2.45</td>
<td>$SO_4^{2-}$</td>
</tr>
<tr>
<td>3</td>
<td>2.70</td>
<td>$NO_3^-$</td>
</tr>
</tbody>
</table>

3.5 Atomic Force Microscope (AFM)

The atomic force microscope (AFM) is a very powerful microscope invented by Binnig, Quate and Gerber (1986). Besides imaging it is also one of the foremost tools for the manipulation of matter at the nanoscale.
The AFM consists of a cantilever with a sharp tip at its end, typically composed of silicon or silicon nitride, with tip sizes on the order of nanometers. The atomic force microscope probes the surface of a sample with a tip, only a couple of microns long and often less than 10 \text{ nm} in diameter at the end. The cantilever is 100-200 \text{ \mu m} long. The tip is brought into close proximity of a sample surface to generate a topographical image. As the tip scans the sample the forces between the tip and the surface cause the cantilever to bend. A detector such as an optical lever measures this deflection and allows a computer to generate a map of the surface topography.

The principal components of an optical lever type atomic force microscope are shown in Fig. 3.8. A laser beam is focused on the reflective gold-plated back of a cantilever and the position of the reflected beam is registered by a position-sensitive photo-detector. As the cantilever bends, the position of the incident laser beam on the detector shifts. The photo-detector can measure displacements of light as small as 1 \text{ nm}. The ratio of the path length between the cantilever and the detector to the length of the cantilever itself produces a mechanical amplification. As a result, the system can detect sub-nanometer vertical movements of the cantilever tip.

Over the years several modes of operation have been developed for the AFM [Bowen et al., 1996a; Bowen et al., 1996b; Bowen et al., 1999]. The primary modes of operation are contact mode, non-contact mode, and dynamic contact mode. In the contact mode operation, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. Bowen et al. (1999) found that the contact mode is inadequate when imaging membranes with small pores such as ultrafiltration and nanofiltration membranes. The reason for this is that diameter of the cantilever tip apex is greater than the pore diameter. When the tip is passed over the small pore the tip can not penetrate into the pore and there is not a great change in cantilever deflection. So to image ultrafiltration and nanofiltration membranes the noncontact mode should be considered. In the noncontact mode, the cantilever is externally oscillated at or close to its resonance frequency. The oscillation gets modified by the tip-sample interaction forces; these changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. A principal advantage of the noncontact mode is that the surface is...
imaged with no contact between the tip and the sample, which is desirable when studying soft membrane surfaces. Samples are not damaged or contaminated through contact with the tip [Bowen et al., 1999].

Because most samples develop a liquid meniscus layer, keeping the probe tip close enough to the sample for these inter-atomic forces to become detectable while preventing the tip from sticking to the surface presents a major hurdle for non-contact mode in ambient conditions. Dynamic contact mode was developed to bypass this problem. In dynamic contact mode, the cantilever is oscillated such that it comes in contact with the sample with each cycle, and then enough force is applied to detach the tip from the sample. Schemes for non-contact and dynamic contact mode operation include frequency modulation and the more common amplitude modulation. In frequency modulation, changes in the oscillation frequency provide information about a sample's characteristics. In amplitude modulation (better known as intermittent contact or tapping mode), changes in the oscillation amplitude yield topographic information about the sample. Additionally, changes in the phase of oscillation under tapping mode can be used to discriminate between different types of materials on the surface.

The AFM has several advantages over the electron microscope. Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true three-dimensional surface profile. Additionally, samples viewed by an AFM do not require any special treatment that would actually destroy the sample and prevent its reuse. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in an ambient or even liquid environment.

The main disadvantage that the AFM has compared to the electron microscope is the image size. The electron microscope can show an area on the order of millimetres by millimetres and a depth of field of the order of millimetres. The AFM can only show a maximum height on the order of micrometres and a maximum area of around 100 by 100 micrometres. Additionally, the AFM can not scan images as fast as an electron microscope. It may take several minutes for a typical region to be scanned.
with the AFM, however an electron microscope is capable of scanning at near real-time (although at relatively low quality).

**Fig. 3.8 Principal components of an optical lever type atomic force microscope**
3.6 Characterisation of the acetate cellulose membranes

Atomic Force Microscope (AFM) was used to visualize the surface structures of the membranes. AFM images provided information about the average pore size, pore distribution and porosity of the membranes.

UFM-50, UFM-100, UFM-200 membranes were imaged using AFM. The average pore size, pore size distribution and porosity were determined for each membrane. The AFM images are represented in Fig. 3.9 (UFM-50), Fig. 3.10 (UFM-100) and Fig. 3.11 (UFM-200); pore size distribution graphs are shown in Fig. 3.12, Fig. 3.13 and Fig. 3.14. Analysing these images (Fig. 3.9, Fig. 3.10 and Fig. 3.11) we calculated the following data: the mean pore size of UFM-50 is 6.29 nm, porosity is 59%; the mean pore size of UFM-100 is 9.5 nm, porosity is 30%; the mean pore size of UFM-200 is 15.1 nm and porosity is 40%. The porosity was calculated using Eq. (3.1).

The experimental data are presented in Appendix I.

\[
\varepsilon = \frac{\pi D_p^2 n}{4S} \times 100 \tag{3.1}
\]

where \(\varepsilon\) is porosity;

\(D_p\) is a membrane pore diameter;

\(n\) is a number of pores;

\(S\) is an area of a membrane.
Fig. 3.9 AFM image for UFM-50

Fig. 3.10 AFM image for UFM-100
Fig. 3.11 AFM image for UFM-200

Fig. 3.12 Pore size distribution scheme for UFM-50
3.7 Polyelectrolytes

A cationic polyelectrolyte poly diallyl dimethylammonium chloride (PDDA, ZETAG 7125) was obtained from CIBA SC (WT) Bradford, West Yorkshire, UK with a molecular weight of 137 kDa (determined by the manufacturer).
An anionic polyelectrolyte poly sodium-4-styrenesulphonate (NaPSS) with molecular weights of 70kDa and 200 kDa was purchased from Aldrich Chemicals, UK. PDDA and NaPSS were prepared as 0.1% aqueous solutions. All of the 0.1% solutions were diluted to the required experimental concentrations within 1-2 days from the preparation.

The chemical structures of the polyelectrolytes are shown in Fig. 3.15.

Fig. 3.15 Chemical Structures of NaPSS (a) and PDDA (b).
3.8 Boron determination

According to the Global Environmental Monitoring System boron can be determined by azomethine-H.

The calibration curve was obtained using solutions prepared diluting a boron standard metal solution 1000 p.p.m. (Fisher scientific). The Azomethine-H solution was prepared using ascorbic acid and Azomethine-H both from Fisher scientific. The buffer solution was prepared using ammonium acetate, glacial acetic and EDTA di-sodium salt produced by Fisher scientific. The pH was monitored by a pH-meter Mettler Toledo 320. The samples were analyzed with a spectrophotometer SHIMADZU.

Azomethine-H solution was made mixing 0.5±0.05 g of azomethine-H and 1±0.05 g of ascorbic acid, dissolving it into 50 ml of water. The freshly made solution was immediately transferred to a plastic bottle. This solution was made up each day than analysis was required.

Buffer solution was prepared dissolving 50±1 g of ammonium acetate in 100 ml of water and adding 25 ml of glacial acetic acid and 1.4±0.06 g of EDTA di-sodium salt.

The analysis was performed according to the following procedure:

1. 10 ml of sample were added with 2.5 ml of buffer solution and 2.5 ml of Azomethine-H solution;
2. the sample was kept at room temperature and in the dark;
3. after one hour the sample was tested in a spectrophotometer at 410 nm with a cell of path-length 10 mm;
4. evaluation of the concentration against a calibration curve.

Samples with the same Boron concentrations but at different concentrations of NaCl were tested to obtain information about the effect of other salts on the analysis: the absorbency was not affected by the present of salts. In Fig. 3.16 shows the determination of the best wavelength made with a boron solution of 0.4 ppm, while an example of a calibration curve is given in Fig. 3.17.
Fig. 3.16 Determination of the best wavelength

Fig. 3.17 Calibration curve of Boron at $\lambda = 410$nm
4.1 Theory

In the dissociation of molecules of a water soluble polymer, superscript 0 is used below for the feed solution.

4.1.1 Dissociation in the feed solution (region 0 in Fig. 2.1)

Each molecule of polyelectrolyte has \( N \) chains (\( N = 5 \) in Fig. 4.1). Let \( i \) be a number of dissociated sites, then \( e_i \) is the charge on this molecule, where \( e \) is the electron charge (\( i = 2 \) in Fig. 4.1). Let \( c_i^0 \) (\( i = 0, 1, \ldots, N \)) be the concentration of polyelectrolyte molecules with \( 0,1,\ldots, N \) dissociated sites. Let \( c^0 \) be the total concentration of polyelectrolyte in the feed solution. Hence, applying conservation law:

\[
c^0_0 + c^0_1 + \ldots + c^0_N = c^0
\]  

\[ (4.1) \]

![Fig. 4.1 Water soluble polymer with N=5 sites capable of dissociation.](image)

The following are the reaction rates for the dissociation and association:

\[
q_0 = -k_p N c_0^0 + K_p c_1^0 \cdot c_1^0
\]

\[
q_1 = -k_p (N - 1)c_1^0 + K_p c_2^0 \cdot 2c_2^0
\]
\[ q_i = -k_p (N-i)c_i^0 + K_p c_i^0 (t+1)c_{i+1}^0 \]  \hspace{1cm} (4.2)

where \( c_i^0 \) is the unknown concentration of chloride ions in the feed solution (to be determined); \( k_p \) and \( K_p \) are dissociation and association reaction constants, respectively (Fig. 4.2). The concentration of chloride ions, \( c_i^0 \), is unknown because part of the ions come from dissociation of a salt (KCl) and the other unknown part comes from dissociation of the polyelectrolyte:

![Diagram of dissociation/association of an individual site](image)

*Fig. 4.2 Dissociation/association of an individual site*

Using equation (4.2) the non-steady state association/dissociation reactions of the polymer can be described by the following system of equations:

\[
\begin{align*}
\frac{dc_0^0}{dt} &= q_0 \\
\frac{dc_1^0}{dt} &= -q_0 + q_1 \\
\frac{dc_N^0}{dt} &= -q_{N-1} \\
\end{align*}
\]

Under steady state conditions all time derivations vanish in equations (4.3), resulting in the following system of algebraic equations:

\[
\begin{align*}
q_0 &= 0 \\
-q_0 + q_1 &= 0 \\
\end{align*}
\]
Rearrangement of system (4.4) gives:

\[ q_0 = 0 \]
\[ q_1 = 0 \]
\[ q_{N-1} = 0 \]

Introducing a dimensionless constant \( \alpha = \frac{k_p}{K_p c_0^0} \), then from equations (4.5) and (4.2) we conclude:

\[ c_i^0 = N \alpha c_0^0 = c_0^0 \alpha C_N^1 \]

\[ c_2^0 = \frac{N-1}{2} \alpha c_1^0 = c_0^0 \alpha^2 \frac{N(N-1)}{2} = c_0^0 \alpha^2 C_N^2 \]

or

\[ c_i^0 = c_0^0 \cdot \alpha^i \cdot C_N^i, \quad i = 1, 2, 3, \ldots, N \]

where \( C_N^i = \frac{N(N-1)\ldots(N-i+1)}{i!} \).

That is all unknown concentrations \( c_i^0 \) (\( i = 1, 2, \ldots N \)) are expressed via only one unknown concentration, \( c_0^0 \), of non-dissociated polyelectrolyte molecules.
To determine unknown concentration $c_o^0$ let us substitute all expressions (4.6) into conservation law (4.1), which results in

$$c_o^0 + c_o^0 \alpha C_N^1 + c_o^0 \alpha^2 C_N^2 + ... + c_o^0 \alpha^N C_N^N = c^0$$

or

$$c_o^0 [1 + \alpha C_N^1 + \alpha^2 C_N^2 + ... + \alpha^N C_N^N] = c^0$$

or $c_o^0 (1 + \alpha)^N = c^0$, that is the concentration of non-dissociated polyelectrolyte molecules, $c_o^0$, is expressed via the total electrolyte concentration, $c^0$, as

$$c_o^0 = \frac{c^0}{(1 + \alpha)^N}$$

(4.7)

According to equations (4.6) and (4.7) all other concentration can be expressed as:

$$c_i^0 = c^0 \frac{\alpha^i C_N^i}{(1 + \alpha)^N}, \quad i = 0, 1, ... N$$

(4.8)

Let us introduce an average value of dissociated sites $\bar{z}^0$ in the feed solution as:

$$\bar{z}^0 = \frac{\sum_{i=1}^{N} i c_i^0}{\sum_{i=0}^{N} c_i^0}$$

(4.9)
where \( \sum_{i=0}^{N} c_i^0 = c^0 \sum_{i=0}^{N} \frac{\alpha^i C_N^i}{(1+\alpha)^N} = \frac{c^0}{(1+\alpha)^N} \sum_{i=0}^{N} \alpha^i C_N^i = c^0 \) \hspace{1cm} (4.10)

as \( (1+\alpha)^N = 1 + N\alpha + \frac{N(N-1)}{2} \alpha^2 + ... = \sum_{i=0}^{N} \alpha^i C_N^i \)

Substitution of expressions (4.7)-(4.8), (4.10) into (4.9) gives:

\[
\frac{c^0}{\sum_{i=1}^{N} i\alpha^i C_N^i} = \frac{\sum_{i=1}^{N} i\alpha^i C_N^i}{c^0(1+\alpha)^N} \hspace{1cm} (4.11)
\]

Concentration of the electrolyte (KCl) is fixed in the feed solution and is equal to \( c^0_+ \).

According to the electroneutrality condition

\[
\sum_{i=1}^{N} i c_i^0 + c^0_+ - c^0_- = 0 \hspace{1cm} (4.12)
\]

Note that the concentration, \( c^0_- \), of chloride ions is to be determined. Substitution of equations (4.7)-(4.8) into Eq. (4.12) results in:

\[
\frac{c^0}{(1+\alpha)^N} \sum_{i=1}^{N} i\alpha^i C_N^i = c^0_+ - c^0_- \hspace{1cm} (4.13)
\]
Let us calculate the sum \( I = \sum_{i=0}^{N} i \alpha^i c^i_N \) in the latter equation. According to the binomial law \((1 + \alpha)^N = 1 + \alpha c_1^1 + \alpha^2 c_2^2 + \ldots + \alpha^N c_N^N\). Differentiation of both sides of the latter expression gives:

\[
N(1 + \alpha)^{N-1} = c_1^1 + 2c_2^2 \alpha + \ldots + NC_N^N \alpha^{N-1}
\]

and multiplying by \( \alpha \):

\[
\alpha N(1 + \alpha)^{N-1} = \alpha c_1^1 + 2c_2^2 \alpha^2 + \ldots + NC_N^N \alpha^N = 1
\]

Hence,

\[
I = \alpha N(1 + \alpha)^{N-1} = \frac{\alpha N}{1 + \alpha} (1 + \alpha)^N
\]  

(4.14)

Using equations (4.13) and (4.14) we conclude:

\[
\frac{c_0 \alpha N}{1 + \alpha} = c_0^\ast - c^\ast
\]  

(4.15)

Let us introduce two dimensionless values \( \alpha^0 = \frac{k_p}{K_p c_0} \) and \( \lambda = \frac{c_0^\ast}{c_0} \). Using these values equation (4.15) can be rewritten as:

\[
\frac{\alpha N}{1 + \alpha} = \frac{\alpha^0}{\alpha} - \lambda
\]  

(4.16)

Equation (4.16) is quadratic equation for determination of the unknown value of \( \alpha \), which can be easily solved. However, we proceed in a different more convenient way. If we divide equation (4.13) by \( c_0^\ast \) and use equation (4.11) we arrive to the following equation:
\[
\overline{z^0} - \frac{c_0}{c^0} + \frac{c_0^0}{c^0} = 0
\]

or

\[
\overline{z} + \lambda = \frac{\alpha^0}{\alpha}
\]

From the latter equation we can determine the unknown value of \(\alpha\) as:

\[
\alpha = \frac{\alpha^0}{\overline{z} + \lambda}
\]  \(\text{(4.17)}\)

where \(\overline{z}^0\) is also an unknown value. Substitution of equation (4.17) into equation (4.16) results in:

\[
\overline{z}^0 + \overline{z}^0(\lambda + \alpha^0) - N\alpha^0 = 0
\]  \(\text{(4.18)}\)

which is an equation for the determination of the average charge.

The solution of the equation (4.18), which should be positive (see Appendix II for details), is:

\[
\frac{\overline{z}^0}{N} = \frac{2}{1 + \frac{\lambda}{\alpha^0} + \sqrt{\left(1 + \frac{\lambda}{\alpha^0}\right)^2 + \frac{4N}{\alpha^0}}} < 1
\]
The latter equation can be rewritten as:

\[
\frac{z^0}{N} = \frac{2}{1 + \frac{c^0 K_p}{k_p} + \sqrt{\left(1 + \frac{c^0 K_p}{k_p}\right)^2 + \frac{4 N K_p c^0}{k_p}}} \tag{4.19}
\]

Equation (4.19) gives the degree of dissociation of polyelectrolyte molecules in the feed solution. If the rate of association is negligible, or the rate of dissociation is much bigger then the rate of association, then equation (4.19) gives \( \frac{z^0}{N} = 1 \), that is, 100% of dissociation. Degree of dissociation according to equation (4.19) decreases with the cation concentration. Note, that it also decreases with the total polyelectrolyte concentration and with the increasing of number of dissociable sites, \( N \).

Summary: the degree of dissociation of polyelectrolyte molecules is completely determined by the ratio of dissociation/association rates, \( k_p / K_p \), which has a dimension of concentration.

4.1.2 Concentration polarization region (1 in Fig. 2.1)

All concentrations are marked by superscript 1 in the concentration polarization region. The concentration in the concentration polarization region depends on the position, \( x \), inside the concentration polarization region and a spontaneous electric field arises inside this region to maintain electroneutrality (see below). Note that \( x = -\delta \) corresponds to the boundary between the feed solution and the concentration polarization region, \( x = 0 \) corresponds to the membrane surface facing the concentration polarization region.

As in the previous section, the conservation law (4.1) for all polyelectrolyte molecules can be rewritten as:

\[
c^0_0(x) + c^1_1(x) + \ldots + c^1_N(x) = c^1(x) \tag{4.20}
\]
where \( c^1(x) \) is the \text{total concentration of the polyelectrolyte}, which is now an unknown function of the position inside the concentration polarization region.

Electroneutrality provides:

\[
\sum_{i=1}^{N} i c^1_i(x) - c^1_- + c^1_+ = 0 \tag{4.21}
\]

As there is no imposed external electric potential difference, the total electric current should vanish:

\[
j_1 + 2j_2 + \cdots + Nj_N - j_+ + j_- = 0 \tag{4.22}
\]

where \( j_i(i=1..N), j_-, j_+ \) are corresponding fluxes of dissociated polyelectrolyte ions, chloride anions and cations, respectively.

The conservation law for each type of polyelectrolyte ions is

\[
\frac{dj_0}{dx} = q_0
\]

\[
\frac{dj_i}{dx} = -q_i + q_0
\]

\[
\frac{dj_N}{dx} = -q_{N-1} \tag{4.23}
\]

All reaction rates in equation (4.23) are given by exactly the same as equation (4.2), where superscript 0 should be replaced by the superscript 1.
The membrane is impermeable to polyelectrolyte molecules and ions, so equation (4.23) should satisfy the following boundary conditions on the membrane surface:

\[ j_0 = j_1 = \ldots = j_N = 0 \quad \text{at } x = 0 \]  \hspace{1cm} (4.24)

Summation of equation (4.22) results in:

\[ \frac{d}{dx} [j_0 + \ldots + j_{N-1}] = 0, \]

or

\[ j_0 + j_1 + \ldots + j_N = \text{const} \]

This constant is zero according to the boundary condition (4.24), for the polyelectrolyte and the latter equation can be rewritten as:

\[ j_0 + j_1 + \ldots + j_N = 0 \]  \hspace{1cm} (4.25)

Note that the latter equation shows that the total flux of the polyelectrolyte molecules vanishes not only on the membrane surface according to the boundary condition (4.24), but everywhere inside the concentration polarization region (equation 4.25).

Conservation law for cations is as follows:

\[ \frac{dj_c}{dx} = 0 \]

hence,
\[ j_{+} = \text{const} \]  \hspace{1cm} (4.26)

Chloride ions obey the following equation:

\[ \frac{dj_{+}}{dx} = -q_{0} - q_{1} - \ldots - q_{N-1} \]  \hspace{1cm} (4.27)

where all association/dissociation reactions are included in the right hand side.

Each of fluxes \( j_{i} \) \((i = 0, \ldots, N)\) is:

\[ j_{i} = v_{i}^{'} - D_{i}(c_{i}^{'} - ic_{i}^{'\phi'}) \]  \hspace{1cm} (4.28)

where \( \phi(x) \) is the spontaneously arising electric field, \( D_{i} \) are diffusion coefficients of polyelectrolyte ions. It is assumed below that all diffusion coefficients \( D_{i} \) independent of the ion charge and the common diffusion coefficient is denoted as \( D \).

After summation of equation (4.25) and using equation (4.28):

\[ v_{i}^{'}(x) - D(c_{i}^{'} - zc_{i}^{'\phi'}) = 0 \]  \hspace{1cm} (4.29)

where \[ z = \frac{\sum_{i=1}^{N} ic_{i}^{'}(x)}{c_{i}^{'}(x)} \]

From equation (4.22) we conclude: \( j_{-} = \sum_{i=1}^{N} ij_{i} + j_{+} \). Differentiation of the latter equation and taking into account equation (4.26) we get:
\[
\frac{d}{dx} \left[ \sum_{i=1}^{N} j_i \right] = - \sum_{i=1}^{N-1} q_i, \tag{4.30}
\]

The sum in the left hand side of equation (4.30) is, \( \sum_{i=1}^{N-1} q_i \):

\[
\sum_{i=1}^{N-1} q_i = (-k_p N c_i^1 + K_p c_i^1 c_i^1) + (-k_p (N-1)c_i^1 + K_p c_i^1 2c_i^2) + \ldots + (-k_p c_{N-1}^1 + K_p c_{N-1}^1 Nc_N^1) =
\]

\[
= -k_p [Nc_i^1 + (N-1)c_i^1 + \ldots + c_{N-1}^1] + K_p c_i^1 (c_i^1 + 2c_2^1 + \ldots + Nc_N^1) = -k_p [N(c_i^1 + c_i^1 + \ldots + c_{N-1}^1)] -
\]

\[
- (c_i^1 + 2c_2^1 + \ldots + (N-1)c_{N-1}^1)] + K_p c_i^1 c_i^1 \bar{z} = -k_p [Nc_i^1 - c_i^1 \bar{z}] + K_p c_i^1 c_i^1 \bar{z}
\]

Using the latter equation in combination with equation (4.30) we conclude:

\[
\frac{d}{dx} j_- = \left[ -kc_i^1 (N - \bar{z}) + Kc_i^1 c_i^1 \bar{z} \right] \tag{4.31}
\]

where:

\[
j_- = wc_i^1 - D_- [c_i^1 - c_i^1 \phi'] \tag{4.32}
\]

Electroneutrality condition (4.21) can be written as:

\[
\bar{z}c_i^1 - c_i^1 + c_i^1 = 0 \tag{4.33}
\]

Finally we get the following system of equations (4.22), (4.26), (4.29) and (4.31), which we rewrite as follows:
\[ w_i^1 - D(c_i^1 + zc_i^1 \phi') = 0 \]  \hspace{1cm} (4.34)

\[ \frac{d}{dx} [w_i^1 - D_i (c_i^1' - c_i^1 \phi')] = c_i^1[k(N - z) - K \bar{z}c_i^1] \]  \hspace{1cm} (4.35)

\[ wc_i^1 - D_i (c_i^1' + c_i^1 \phi') = j_i = \text{const} \]  \hspace{1cm} (4.36)

\[ \sum_{i=1}^{N} i j_i - j^- + j^+ = 0 \]  \hspace{1cm} (4.37)

and electroneutrality condition (4.33).

Equation (4.37) can be rewritten as:

\[ \nu \sum_{i=1}^{N} ic_i^1 - D \left[ \left( \sum_{i=1}^{N} i c_i^1 \right)' + \left( \sum_{i=1}^{N} i^2 c_i \phi' \right) \right] - [w_i^1 - D_i (c_i^1' - c_i^1 \phi')] + j_i = 0 \]

or

\[ \nu \bar{z}c - D \left[ (\bar{z}c') + z^2 c \phi^1 \right] = wc_i - D_i (c_i^1' - c_i^1 \phi') - j_i \]  \hspace{1cm} (4.38)

Assuming N\textgreater\textgreater 1 in accordance with our experimental condition.

The value \( z \), which can be represented as a sum, can be introduced:

\[ z = z_1 + z_2 + \ldots + z_N \]

where random values \( z_i (i = 1 \ldots N) \) are equal to 1 if the corresponding site is in the dissociated state and equal to 0 if it is in non-dissociated state. All random values \( z_1 \ldots z_N \) are assumed to be independent random variables. Let \( p \) be the probability that
\( z_i = 1 \) \((i = 1 \ldots N)\) (dissociated) and \(1 - p\) is the probability that \( z_i = 0 \) \((i = 1 \ldots N)\) (nondissociated). Consequently:

\[
\overline{z} = Nz_1 = Np
\]  

(4.39)

Variance is \(\left(z - \overline{z}^2\right) = \overline{z^2} - \overline{z}^2 = Np(1 - p)\). Hence, \(\frac{\overline{z^2}}{\overline{z}} = 1 + \frac{1-p}{pN}\) and

\[
\left(\frac{\overline{z^2}}{\overline{z}} - 1\right) = \frac{1-p}{pN} \ll 1 \text{ at } N \gg 1
\]

Hence at \(N \gg 1\) we can use the following equality:

\[
\overline{z^2} = \overline{z}
\]  

(4.40)

Substitution of equation (4.40) into equation (4.38) results in:

\[
\nu z^c - D\left[(z c)^1 + \overline{z^2 c^1} \varphi\right] = \nu c - D\left(c^1 - c^1 \varphi\right) - j
\]  

(4.41)

Now the system of five equations (4.33)-(4.36) and (4.41) includes five unknown functions \(c^1(x), \varphi(x), c^1(x), c^1(x), \overline{z}(x)\).

Boundary conditions at \(x = -\delta\):

\[
c^1(-\delta) = c^0
\]

\[
c^1(-\delta) = c^0
\]

\[
c^1(-\delta) = c^0
\]  

(4.42)
The problem under investigation, inside the second region (Fig. 2.1), is solved under the following simplifying assumptions:

1. The degree of dissociation of polyelectrolyte molecules remains constant inside the concentration polarization region 2 (Fig. 2.1) and equal to its value inside the feed solution according to Equation (4.19). The latter means that the average charge of polyelectrolyte molecules, \( \bar{z} \), remains constant.

2. The concentration of cations is substantially smaller than the concentration of chloride anions.

Under these assumptions the previous system of equations is substantially simplified and can be presented as a solution of two independent problems inside the concentration polarization region 2 (Fig. 2.1):

(a) Flow and diffusion of the polyelectrolyte:

\[
0 = \nabla c^1 - D \left( c^1 + \bar{z} c^1 \varphi' \right) \tag{4.43}
\]

\[
0 = \nabla c^- - D_\subset c^- \left( c^- + \bar{z} c^- \varphi' \right) \tag{4.44}
\]

\[
\bar{z} c^1 = c^- \tag{4.45}
\]

(b) Flow and diffusion of cations in the electric field created by the flow and diffusion of the polyelectrolyte provided by part (a) above.
Problem (a) equations (4.43)-(4.45) can be directly solved. Equations (4.43)-(4.44) can be rewritten and integrated using boundary conditions (4.42) as:

\[
\frac{\nu}{D} = \left(\ln c^1\right)' + z\varphi'
\]

\[
\frac{\nu}{D} (x + \delta) = \ln \frac{c^1}{c_0^1} + z\varphi
\]

(4.46)

\[
\frac{\nu}{D} = \left(\ln c^-^1\right)' - \varphi'
\]

\[
\frac{\nu}{D^-} (x + \delta) = \ln \frac{c^1}{c_0^-} - \varphi
\]

(4.47)

In order to maintain electroneutrality in the feed solution, for problem (a):

\[
c_0^- = z c_0
\]

and for electroneutrality (4.45) we conclude:

\[
\frac{c^1^-}{c_0^-} = \frac{z c^1}{z c_0^0} = \frac{c^1}{c_0}
\]

Substitution of the latter expression into equations (4.46)-(4.47) determines the electric potential distribution in the concentration polarization region 2 (Fig. 2.1):

\[
\varphi = \nu \left(\frac{1}{D} - \frac{1}{D^-}\right) \frac{1}{z + 1} (x + \delta)
\]

(4.48)

and the polyelectrolyte concentration profile:

\[
\nu \left(\frac{1}{Dz} + \frac{1}{D^-}\right) (x + \delta) = \left(1 + \frac{1}{z}\right) \ln \frac{c^1}{c_0}
\]

or
\[ c^1(x) = c^0 \exp \left\{ \frac{v(x + \delta)}{D_d} \right\} \]  \hfill (4.49)

where \[ \frac{1}{D_d} = \frac{1}{D_+} + \frac{1}{\bar{D} + \frac{1}{\bar{D}}} \]

According to equation (4.48) the electric potential inside the concentration polarization region 2 (Fig. 2.1) changes linearly with \( x \).

Using equation (4.49) and the electroneutrality condition (4.45) we can determine the concentration of chloride ions on the membrane surface, \( c^1(0-) \):

\[ c^1(0-) = \bar{z}c^0 \exp \left\{ \frac{v\delta}{D_d} \right\} \]  \hfill (4.50)

Returning to problem (b): flow and diffusion of cations obeys equation (4.36), where the electric potential distribution is given by equation (4.48). Substitution of electric potential distribution from equation (4.48) into equation (4.36) results in:

\[ j_+ = \nu c^1_+ - D_+(c^1_+ + c^1_\nu \frac{1}{\bar{z} + 1} \left( \frac{1}{D} - \frac{1}{D} \right)) \]

or

\[ j_+ = \nu(1 + \omega)c^1_+ - D_+ c^1_\nu, \quad \omega = \frac{D_+}{\bar{z} + 1} \left( 1 - \frac{1}{D} \right) > 0 \]  \hfill (4.51)

Equation (4.51) shows that presence of polyelectrolyte ions in the concentration polarization region results in an enhancing of the convective transport of cations. Solution of equation (4.51) subject to the boundary condition:
results in the following expression for the cation concentration on the membrane surface from the feed solution side, \( c_+^\prime (0-) \):

\[
c_+^\prime (0-) = \frac{j_+}{v(1+\omega)} + \left( c_+^0 - \frac{j_+}{v(1+\omega)} \right) e^{\frac{v(1+\omega)}{D_+} \delta}
\]

(4.53)

where the flux, \( j_\nu \), is to be determined.

### 4.1.3 Ion transfer inside the membrane (2 in Fig. 2.1)

Inside the membrane all concentrations are left without superscript. It is necessary to solve ion transfer inside the membrane, \( 0 < x < h \).

Inside the membrane the flow and diffusion of cations and anions is described by the following equations:

\[
j_+ = \beta_+ v e_+ - D_+^2 (c_+^\prime + c_+ \varphi') = \text{const}
\]

(4.54)

\[
j_- = \beta_- v e_- - D_-^2 (c_-^\prime - c_- \varphi') = \text{const}
\]

(4.55)

where \( \beta_+ \), \( \beta_- \) are deviation of the average convective velocity of cations and anions, respectively, from the filtration velocity of water inside the membrane (Starov and Churaev, 1993).

To maintain electroneutrality:

\[
c_+ - c_- = 0
\]

(4.56)
There is no external electric potential difference, hence, the total electric current should vanish:

\[ j_+ - j_- = 0 \]  \hspace{1cm} (4.57)

Equation (4.55) can be rewritten using the latter two equations as:

\[ j_+ = \beta_- v c_+ - D^2 (c'_+ - c_+ \phi') \]  \hspace{1cm} (4.58)

Now the electric potential, \( \phi' \), can be excluded from the system of Equations (4.54), (4.58) and:

\[ c'_+ = v c_+ \frac{\beta_-}{D} - \frac{j_+}{D} \]  \hspace{1cm} (4.59)

where

\[ \frac{\beta_-}{D} = \frac{\frac{\beta_+}{D^2} + \frac{\beta_-}{D^2}}{2}, \quad \frac{1}{D} = \frac{1}{D^2} + \frac{1}{D^2} \]

Let \( c_+(0+) \) be an unknown concentration on the membrane surface from the membrane side, then the solution of Eq. (4.59) is:

\[ c_+(x) = \frac{j_+}{\beta_- v} + \left[ c_+(0+) - \frac{j_+}{\beta_- v} \right] \exp \left\{ \frac{\beta_-}{D} v x \right\} \]  \hspace{1cm} (4.60)

where \( \overline{\beta} = \overline{D} \frac{\beta}{D} \). Note that because of the concentration jump on the membrane surface (Starov and Churaev, 1993), \( c'_+(0-) \neq c_+(0+) \). The latter jump is calculated below using the equality of chemical potentials at the membrane surface (see below).

Two unknown values \( c_+(0+) \) and \( j_+ \) are determined below.

Equality of chemical potentials at the membrane surface reads (Starov and Churaev, 1993):
\begin{align}
    c^+(0-) &= c^-(0+) \gamma^+ \exp(\Delta \varphi') \\
    c^-(0-) &= c^+(0+) \gamma^- \exp(-\Delta \varphi')
\end{align} \tag{4.61}
\tag{4.62}

where \( \gamma^\pm = \exp(\Phi^\pm) \) are the distribution coefficients, \( \Phi^\pm \) are dimensionless (in \( kT \) units) potentials of specific interactions of ions with the membrane material; \( \Delta \varphi^0 \) is the electric potential jump across the membrane surface, \( x = 0 \).

The latter conditions should be combined with the electroneutrality condition:

\[ c^+(0+) = c^-(0+) \] \tag{4.63}

After some rearrangement we can conclude from Equations (4.61)-(4.63):

\[ c^+(0+) = \frac{[c^+(0-) \cdot c^-(0-)]^{0.5}}{\gamma} \] \tag{4.64}

where \( \gamma = \gamma^+ \gamma^- \).

Using expressions for concentration on the membrane surface from the feed solution side (4.50) and (4.53) and equation (4.64) can be rewritten as:

\[ c^+(0+) = \frac{1}{\gamma} \sqrt{c^0 \exp\left[ \frac{v \delta}{D_+} \right] \sqrt{\frac{j^+}{v(1+\omega)} + \left( c^0 - \frac{j^+}{v(1+\omega)} \right) \exp\left[ \frac{v(1+\omega)}{D_+} \delta \right]}} \] \tag{4.65}
Equality of chemical potentials and flow conditions at the second membrane surface \((x = h)\) provides:

\[
c_+(h-)\gamma_+ \exp(z_+\Delta \phi^2) = c_3^+ \tag{4.66}
\]

\[
c_-(h-)\gamma_- \exp(-\Delta \phi^2) = c_3^- \tag{4.67}
\]

where \(c_3^+, c_3^-\), \(\Delta \phi^2\) are concentrations of cations, anions in the permeate and electric potential jump across the membrane surface, \(x = h\), respectively.

The flow condition gives the following expressions for the concentrations in the permeate solution:

\[
c_3^+ = \frac{j_+}{\nu} \tag{4.68}
\]

Note superscript 3 marks the permeate solution. Electroneutrality condition reads:

\[
c_+(h-) - c_-(h-) = 0 \tag{4.69}
\]

Using equations (4.69), (4.66), (4.67) and rearrangement provides:

\[
c_+(h-) = \frac{j_+}{\nu \gamma} \tag{4.70}
\]

where \(\gamma = \gamma_-^{0.5} \gamma_+^{0.5}\). Using equation (4.60):

\[
c_+(h-) = \frac{j_+}{\alpha \nu} + [c_+(0+) - \frac{j_+}{\alpha \nu}] e^{\frac{\gamma_0 h}{\alpha}} \tag{4.71}
\]

From equations (4.70)-(4.71):
\[ j_+ = \frac{\nu c_+ (0+) \gamma}{1 + (\gamma - 1) \left(1 - e^{-\frac{\alpha}{D_c}}\right)} \]  

(4.72)

where \( \gamma = \frac{\nu}{\alpha} \) and concentration \( c_+ (0+) \) is given by equation (4.65), which should be substituted into equation (4.72).

That gives the required equation for the determination of the unknown flux \( j_+ \):

\[ j_+ = \frac{\frac{1}{v} \sqrt{\frac{v \delta}{D_e}} \left( \frac{j_+}{v(1 + \omega)} + \frac{c_+ - j_+}{v(1 + \omega)} \right) \exp \left\{ \frac{v(1 + \omega) \delta}{D_e} \right\}}{1 + (\gamma - 1) \left(1 - e^{-\frac{\alpha}{D_c}}\right)} \]  

(4.73)

Dividing both sides of the latter equation by \( c_+^0 \) and introducing a new unknown dimensionless value, \( \Lambda = \frac{j_+}{v c_+^0} \), which is equal to the ratio of the cation concentration in the permeate to the concentration in the feed solution. Using this new unknown value equation (4.73) can be rewritten as:

\[
\Lambda^2 = \frac{\frac{\Lambda}{(1 + \omega)} + \left(1 - \frac{\Lambda}{(1 + \omega)}\right) \exp \left\{ \frac{v(1 + \omega) \delta}{D_e} \right\}}{\left[\frac{c_+^0 \exp \left\{ -\frac{v \delta}{D_e} \right\}}{\sqrt{\frac{v \delta}{D_e}}} \right]^2 \left[1 + (\gamma - 1) \left(1 - e^{-\frac{\alpha}{D_c}}\right)\right]^2}
\]

The positive solution of the latter equation is:
\( \Lambda = \frac{2(1 + \omega)}{\sqrt{(1 - \exp(-P_e))^2 + 4A \exp(-P_e)(1 + \omega)^2 + 1 - \exp(-P_e)}} \)  \hspace{1cm} (4.74)

\[ A = \left[ \frac{c^0}{z c^0} \exp\left(-\frac{v D_e}{D_f}\right) \right]^{1+\left[\left(1 - \frac{\bar{z}}{z^0}\right)^2\right]} \left[1 + \left(1 - \frac{\bar{z}}{z^0}\right) \left(1 - e^{-\frac{D_e}{D_f}}\right)\right] \]

where \( P_e \) is the outer Peclet number.

Note that the rejection coefficient \( R = 1 - \Lambda \). We refer below to \( \Lambda \) as the degree of concentration in the permeate solution or simply as degree of concentration.

If velocity, \( v \), tends to zero, that is \( P_e \ll 1 \), then according to equation (4.74):

\[ \Lambda|_{v \to 0} = \sqrt{\frac{z c^0}{c^0}} \]  \hspace{1cm} (4.75)

i.e. independent of the membrane rejection properties and increasing with degree of dissociation of the polymer, \( \bar{z} \), polymer concentration in the feed solution, \( c^0 \), and decreasing with the concentration of cations in the feed solution. According to our assumptions \( \Lambda \) in equation (4.75) is bigger than 1 (a negative rejection).

If velocity \( v \to \infty \), that is \( P_e \gg 1 \), then we conclude using equation (4.74):

\[ \Lambda|_{v \to \infty} = 1 + \omega \]  \hspace{1cm} (4.76)

According to the definition of \( \omega \), \( \omega = \frac{D^+}{\bar{z} + 1} \left( \frac{1}{D^+} - \frac{1}{D^-} \right) > 0 \).
To deduce the dependency of $A$ on the filtration velocity, $v$, we rewrite expression for $A$ in equation (4.74) as follows:

$$A = \left[ \frac{c^0}{z c^0} \exp\{-aPe\} \right] \left[ 1 + \left( \frac{\gamma - 1}{1 - \exp\{-bPe\}} \right) \right]^2,$$

$$Pe = \frac{v(1 + \omega)}{D_z ^*}, \quad b = \frac{D_z h}{D (1 + \omega) \delta}, \quad a = \frac{D_z}{(1 + \omega) D_z ^*}$$

If $\gamma = 1$, that is the membrane does not reject cations at all (but still completely rejects polyelectrolyte), then $A$ according to equation (4.74) decreases from the maximum value given by equation (4.75), which is much bigger than 1, to the minimum value given by equation (4.76).

### 4.1.4 Filtration velocity and applied pressure difference

In this part filtration through a membrane in the presence of a polyelectrolyte solution (without added $KCl$) at different concentration is considered. A critical concentration of the polyelectrolyte, below which a gel layer on the membrane does not form, is derived.

Concentration of the polyelectrolyte on the membrane surface is given by Eq. (4.49), which can be rewritten as:

$$c^0_m = c^0 \cdot \exp\{Pe_m\} \quad (4.77)$$

where $Pe_m = \frac{\nu \delta}{D_{ef}}$.

Filtration velocity taking into account the osmotic pressure is:

$$v = K_m \Delta p - c^1_m R T = K_m \Delta p - K_m c^0 R T e^{Pe}$$
where $\Delta p$ is the applied pressure difference, $K_m$ is the permeability of the active layer of the membrane. Thus:

$$Pe_m = \frac{v\delta}{D_d} = \frac{K_m \Delta p \delta}{D_d} - \frac{K_m c^0 RT \delta}{D_d} \exp\{Pe_m\}$$

or

$$Pe_m = Pe_o - \chi \exp\{Pe_m\}$$  \hspace{1cm} (4.78)

where $Pe_o = \frac{K_m \Delta p \delta}{D_{et}}$ (dimensionless filtration velocity in the absence of concentration polarization), $\chi = \frac{K_m c^0 RT \delta}{D_d}$.

Equation (4.78) is a non-linear equation for determination of the dimensionless filtration velocity $Pe_m$. The latter equation can be rewritten as:

$$Pe_o = Pe_m + \chi \exp\{Pe_m\}$$  \hspace{1cm} (4.79)

that is as a reverse function of the dimensionless applied pressure difference, $Pe_o$, on the dimensionless filtration velocity, $Pe_m$. The latter dependency is shown in Fig. 4.3. Rotation of the latter figure gives the required dependency of the dimensionless filtration velocity, $Pe_m$, on the dimensionless pressure, $Pe_o$ (Fig. 4.4)
Fig. 4.3 Dimensionless pressure on the dimensionless filtration velocity according to equation (4.79)

Fig. 4.4 The inverse dependency as compared with Fig. 4.3.

Note the filtration velocity can be easily obtained using Fig. 4.4 as:
\[ v = Pe_m \cdot \frac{D}{\delta} \]

The filtration process proceeds in the way described above until the concentration on the membrane surface (Eq. (4.77)) reaches the concentration of gel-layer formation, \( c_q \). Fig. 4.5 shows the procedure for the critical pressure determination:

\[ c^0 \exp\{Pe_{cr}\} = c_q \quad (4.80) \]

or

\[ Pe_{cr} = \ln \frac{c_q}{c^0} \quad (4.81) \]

Using Eq. (4.80) the latter equation takes the following form:

\[ Pe_{cr} + \chi e^{Pe_{cr}} = \frac{K_m \delta}{D_{ef}} \Delta p_{cr} \]

or after substitution of Eq.(4.81):

\[ \Delta p_{cr} = \left[ \ln \frac{c_q}{c_0} + \chi \frac{c_q}{c_0} \right] \cdot \frac{D_{ef}}{K_m \delta} \quad (4.82) \]

which determines the critical applied pressure.
Fig. 4.5 Determination of the critical pressure difference

If $\Delta p > \Delta p_c$, then a gel layer forms:

$c'(-l) = c_g$

where $l$ is an unknown thickness of the gel layer. Using Eq. (4.49) the equation

$v(S-R)$

becomes:

$c_g = c^0 e^{D_{ef}},$ or

$\ln \frac{c_g}{c_0} = \frac{v(\delta - l)}{D_{ef}}$ \hspace{1cm} (4.83)

If the thickness of the gel-layer is much smaller than the thickness of the concentration polarization layer, $l << \delta$, then according to Eq. (4.83) the filtration velocity remains constant.
\[ v_{\text{sm}} = \frac{D_s}{\delta} \ln \frac{c_0}{c^b} \]  \hspace{1cm} (4.84)

That is, the dependency of the filtration velocity, \( v \), on the applied pressure has the form presented in Fig. 4.6.

\[ \begin{align*}
\nu & \quad \nu_{\text{lim}} \\
\Delta p & \\
\end{align*} \]

Fig. 4.6 Filtration velocity on the applied pressure difference

In the following analysis only pressures \( \Delta p < \Delta p_{\text{cr}} \) are considered, because the cake provides an additional rejection to dissolved ions, which must be avoided for the concentration of solute within the permeate process to work.
CHAPTER 5: EXPERIMENTAL DETERMINATION OF MODEL PARAMETERS

5.1 Introduction

In this Chapter a new method of a polyelectrolyte charge determination is presented. The method is based on conductivity measurements that allows directly to estimate the polyelectrolyte diffusion coefficient, which is subsequently used to extract the polyelectrolyte charge. Knowing the value of the charge is essential to predict the degree of concentration in the permeate according to the theory described in Chapter 4 (equation (4.74)).

A method to determine model parameters \( a, b \) and \( g \) from Eq. (4.74) independently are proposed here.

5.2 Materials and methods

All conductivity experiments presented here were carried out at 20 °C. The conductivity meter used was Precision Component Analyzer 6425 (WAYNE KERR) with 0.02 % measurement accuracy. In order to avoid problems of electrode polarization, the conductivity of the solutions was measured at different frequencies and extrapolated to zero. The frequency range used was from 20 Hz to 300 kHz. At each frequency the solution had been maintained for 15-20 minutes to reach equilibrium and after that the conductivity measurements were taken. The conductivity cell constant \( (C) \) was determined measuring the conductivity of a standard solution of KCl \( 10^{-2} \text{ mol/l} \) of the known conductivity. The cell constant is equal to the distance between the parallel electrodes \( (l) \) divided by the cross-sectional area of the electrodes \( (A) \):

\[
C = \frac{l}{A}
\]

PDDA with molecular weight of 137 kDa and NaPSS with molecular weights of 70 kDa and 200 kDa were used in the conductivity experiments. Solutions of PDDA and NaPSS polyelectrolytes at concentrations of 0.1; 0.25; 0.5; 0.75; 1.0; 2.5; 5.0 g/l,
were prepared and their conductivities were measured. The conductivities of mixtures of the polyelectrolyte solutions (1.0 g/l) with KCl solutions of different concentrations in the range of $10^{-6}$-$10^{-2}$ mol/l were also measured.

5.3 Polyelectrolyte charge and diffusion coefficient determination

The diffusion coefficient of each polyelectrolyte has been determined measuring conductivity and using the following equation:

$$\sigma = \frac{F^2}{RT} \left( z^2 c_0 D - z c_0 D_\text{-} \right)$$  \hspace{1cm} (5.1)

where $\sigma$ is conductivity

$c_0$ is a polyelectrolyte concentration;

$z$ is a polyelectrolyte charge;

$D$ is a polyelectrolyte diffusion coefficient;

$D_\text{-}$ is the anion diffusion coefficient;

$F$ is the Faraday constant;

$R$ is the gas constant;

$T$ is temperature.

Introducing the new parameter $A = \frac{F^2}{RT} \left( z^2 D - z D_\text{-} \right)$, equation (5.1) can be rewritten as:

$$\sigma = A c_0$$  \hspace{1cm} (5.2)

From conductivity measurements the value of $A$ can be found as the slope of the linear part of the curves in Fig. 5.1, Fig. 5.2 and Fig. 5.3. In Fig. 5.1 the conductivity data of PDDA at different concentrations are presented. In Fig. 5.2 and Fig. 5.3 the same dependences are shown for NaPSS with different molecular weight. If the value of $A$ is known for each polyelectrolyte, their diffusion coefficients can be determined.
Fig. 5.1 Conductivity data at different PDDA concentrations

\[ \sigma = 67212c_0 \]

Fig. 5.2 Conductivity data at different NaPSS concentrations with a molecular weight of 70 kDa.

\[ \sigma = 48731c_0 \]
Fig. 5.3 Conductivity data at different NaPSS concentrations with a molecular weight of 200 kDa.

Using equation (4.19) for a solution of a pure polyelectrolyte:

\[ z = \frac{2N}{1 + \sqrt{1 + \frac{4Nc_0}{c^*}}} \]  

(5.3)

Where:
N is the number of monomers,
c* is the ratio of \( K_p \) and \( k_p \) that are association and dissociation reaction constants.

Substituting equation (5.3) in equation (5.1), the following is obtained:

\[ \sigma = \frac{F^2c_0}{RT} \left( \frac{4N^2D}{1 + \frac{4Nc_0}{c^*} + 2\sqrt{1 + \frac{4Nc_0}{c^*}}} + \frac{2ND_-}{1 + \sqrt{1 + \frac{4Nc_0}{c^*}}} \right) \]  

(5.4)
which can be rearranged as:

$$\sigma = \frac{F^2 c_0}{RT} \left( \frac{2N^2 D}{1 + \frac{2Nc_0}{c^*} + \sqrt{1 + \frac{4Nc_0}{c^*}}} + \frac{2ND}{1 + \sqrt{1 + \frac{4Nc_0}{c^*}}} \right)$$  \hspace{1cm} (5.5)$$

and subsequently as:

$$\frac{\sigma RT}{2F^2 Nc_0} = \left( \frac{ND}{1 + \frac{2Nc_0}{c^*} + \sqrt{1 + \frac{4Nc_0}{c^*}}} + \frac{D_o}{1 + \sqrt{1 + \frac{4Nc_0}{c^*}}} \right)$$  \hspace{1cm} (5.6)$$

Let us introduce the following constant, $B = \frac{RT}{2F^2 N}$, which can be calculated for each individual polyelectrolyte. Using this constant and the latter equation it is possible to calculate $z$ for each polyelectrolyte from experimental data. Equation (5.6) can be rearranged using the following identity:

$$\left( 1 + \sqrt{1 + \frac{4Nc_0}{c^*}} \right)^2 = 1 + 1 + \frac{4Nc_0}{c^*} + 2 \sqrt{1 + \frac{4Nc_0}{c^*}} = 2 \left( 1 + \frac{2Nc_0}{c^*} + \sqrt{1 + \frac{4Nc_0}{c^*}} \right)$$

Introducing $y = 1 + \sqrt{1 + \frac{4Nc_0}{c^*}}$ and $\frac{y^2}{2} = 1 + \frac{2Nc_0}{c^*} + \sqrt{1 + \frac{4Nc_0}{c^*}}$

Equation (5.6) can be rewritten as:

$$\frac{\sigma B}{c_0} = \frac{2ND}{y^2} + \frac{D_o}{y}$$  \hspace{1cm} (5.7)$$

Making simple rearrangements of the latter equation we arrive to:

$$\frac{\sigma B}{c_0} y^2 = 2ND + D_o y$$
\[
\frac{\sigma B}{c_0} y^2 - D_y - 2ND = 0
\]

Solutions of the latter equation are:

\[
y_{1,2} = \frac{-D_y \pm \sqrt{D_y^2 + 8ND \frac{\sigma B}{c_0}}}{2 \frac{\sigma B}{c_0}}, \text{ it should be } y > 0
\]

(5.8)

As only the positive root is of interest here, hence, the solution is:

\[
y = \frac{D_y + \sqrt{D_y^2 + 8ND \frac{\sigma B}{c_0}}}{2 \frac{\sigma B}{c_0}} = 1 + \sqrt{1 + \frac{4Nc_0}{c^*}} \text{ or}
\]

\[
y = \frac{D_y c_0 + \sqrt{D_y^2 c_0^2 + 8ND\sigma Bc_0}}{2\sigma B}
\]

(5.9)

The latter equation can be rewritten as:

\[
Y = (y - 1)^2 = 1 + \frac{4Nc_0}{c^*}
\]

(5.10)

hence, a linear function of the polyelectrolyte concentration, which starts at 1 at zero polyelectrolyte concentration. The latter equation includes only one unknown constant \(c^*\), which has dimension of concentration and it is the main equation for determination of the latter unknown constant.

From conductivity experimental data the value \(Y_{exp}\) can be calculated using equations (5.9) and (5.10); from the plot of \(Y_{exp}\) against \(c_0\), \(c^*\) can be determined for each polyelectrolyte from the slope of the linear part in the Fig. 5.5 and Fig. 5.6. In Table 5.1 values of calculated \(c^*\) and \(D\) for each polyelectrolyte are presented. In Fig. 5.7, Fig. 5.8, Fig. 5.9 a dependence of \(\sigma B/c_0\) as a function of a polyelectrolyte concentration is shown, \(\sigma B/c_0\) is decreasing respectively with a polyelectrolyte concentration increasing.
Table 5.1 Calculated values of $c^*$ and $D$ for each polyelectrolyte

<table>
<thead>
<tr>
<th>Polyelectrolyte</th>
<th>$c^*$, mol/l</th>
<th>$D$, cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDDA</td>
<td>0.014</td>
<td>$3 \times 10^{-9}$</td>
</tr>
<tr>
<td>NaPSS (MW 200 kDa)</td>
<td>0.041</td>
<td>$1.85 \times 10^{-9}$</td>
</tr>
<tr>
<td>NaPSS (MW 70 kDa)</td>
<td>0.074</td>
<td>$6.3 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

Fig. 5.4 $Y$ as a function of PDDA concentration
Fig. 5.5 $Y$ as a function of NaPSS concentration.

Fig. 5.6 $Y$ as a function of NaPSS concentration.
Fig. 5.7 $\sigma \cdot B / c_0$ as a function of PDDA concentration

Fig. 5.8 $\sigma \cdot B / c_0$ as a function of NaPSS (200 kDa) concentration
In case the diffusion coefficient and $c^*$ for each polyelectrolyte are known, it is possible to predict the conductivity of a mixture of a polyelectrolyte with KCl using equation (5.6).

In Fig. 5.10 and Fig. 5.11 conductivity of a mixture of a polyelectrolyte (1.0 g/l) with KCl as a function of KCl concentration is presented. These experimental data are in a good agreement with the model prediction of Eq. 5.6. Solid lines are drawn according to the theoretical equation (5.6) where both constants $D$ and $c^*$ have been determined according to the above procedure.

Diffusion coefficient determined for NaPSS with molecular weight 70 kDa was compared with a diffusion coefficient for NaPSS with molecular weight 10 kDa from the literature [Gruner et al., 1981]. In this work the dynamics of Na-polystyrene sulphonate (Na-PSS) in water at low ionic strength was investigated by photon correlation spectroscopy; the diffusion coefficient of NaPSS was measured in the dilute regime where the polyelectrolyte concentration was varied from 0.1 g/l to 5.0 g/l. The value obtained for the diffusion coefficient was $6.7 \times 10^{-8}$ cm$^2$/s, which is close to the value of the diffusion coefficient found here for NaPSS with a molecular weight 70 kDa from conductivity experiments.

Fig. 5.12 shows the PDDA charge in the form of $z/N$ as a function of the polyelectrolyte concentration in the presence of $10^{-4}$ mol/l KCl. The polyelectrolyte charge was calculated using
the previously found value for $c^*$. It is evident from the Fig. 5.12 that, with the polyelectrolyte concentration increasing, the ratio of dissociation is gradually decreasing.

This result supports the fact that the negative rejection of salts in the presence of a polyelectrolyte decreases at high polyelectrolyte concentrations (see Chapter 6).

![Graph of conductivity as a function of KCl concentration at the presence of PDDA 1.0 g/l.](image)

**Fig. 5.10** Conductivity as a function of KCl concentration at the presence of PDDA 1.0 g/l.
Fig. 5.11 Conductivity as a function of KCl concentration at the presence of NaPSS (200 kDa) 1.0 g/l.

Fig. 5.12 $z/N$ as a function of PDDA concentration in the presence of $10^{-4}$ mol/l KCl
5.4 Model parameters (a, b, g) determination

Filtration results of KCl solutions at different concentrations through UFM-50, UFM-100 and UFM-200 membranes are presented in Fig. 5.13, Fig. 5.14 and Fig. 5.15. In all cases significant potassium rejections were observed. However these graphs plotted as dependences of rejection coefficients \( R \) against filtration velocities are not so characteristic. To make these dependences more distinctive, a new function 
\[ f = \frac{R}{1-R} \]
was introduced and the graphs were replotted using the function \( f \), which assists the determination of the maximum values of rejection coefficients. Introducing new parameters \( a = \frac{\delta}{D_+}, \ b = \frac{\alpha h}{D_m}, \ g = \gamma - 1 \) and applying the following equation, which is derived from the theory proposed by Starov and Churaev (1993):

\[ f = ge^{-av opt}(1-e^{-bV opt}) \]  
(5.11)

We can express these coefficients as:

\[ g = \frac{f_{max}}{e^{-av_{opt}}(1-e^{-bV_{opt}})} \]

\[ a = \frac{b}{e^{bV_{opt}} - 1} \]

where \( b \) is the only one fitting parameter. Here,

\( \gamma \) is a distribution coefficient which is a ratio between the ion concentration in the bulk and inside a membrane pore:

\( \delta \) is a laminar boundary layer thickness;

\( \alpha \) is a deviation of ion convective velocity from solution convective velocity in the membrane;
is a membrane active layer thickness; 

$D_+$ is a diffusion coefficient of a cation; 

$D_m$ is a diffusion coefficient of ions inside the membrane. 

$f_{\text{max}}$ is maximum of $f$ function corresponding to the optimum filtration velocity $v_{\text{opt}}$. 

Function $f$ via filtration velocity is shown in Fig. 5.16, Fig. 5.17 and Fig. 5.18. Theoretical curves were plotted according to Eq. 5.11. From experimental data $f_{\text{max}}$ and $v_{\text{opt}}$ were estimated and summarised in Table 5.2 for each case. In Table 5.3 values of parameters $a$, $b$ and $g$ are presented for each membrane. The values of these parameters, obtained for the 5 nm pore size membrane, are in the same order of magnitude of data reported for 2-3 nm nanofiltration membranes (Starov and Churaev 1993). 

<table>
<thead>
<tr>
<th>Membrane pore size (nm)</th>
<th>5</th>
<th>5</th>
<th>5</th>
<th>10</th>
<th>10</th>
<th>20</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of KCl (mol/l)</td>
<td>$10^4$</td>
<td>$5*10^{-4}$</td>
<td>$10^{-3}$</td>
<td>$10^5$</td>
<td>$10^4$</td>
<td>$10^5$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>$f_{\text{max}}$</td>
<td>4.41</td>
<td>1.63</td>
<td>0.67</td>
<td>0.89</td>
<td>0.59</td>
<td>0.58</td>
<td>0.45</td>
</tr>
<tr>
<td>$v_{\text{opt}}$ ($\mu$m/s)</td>
<td>15.23</td>
<td>19.26</td>
<td>14.81</td>
<td>15.44</td>
<td>13.23</td>
<td>14.78</td>
<td>11.00</td>
</tr>
</tbody>
</table>
Table 5.3 Values of \( a \), \( b \) and \( g \) parameters for each membrane

<table>
<thead>
<tr>
<th>Membrane pore size (nm)</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (s/cm)</td>
<td>15</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>( b ) (s/cm)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>( g )</td>
<td>26</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

In case of UFM-50 membrane substantial potassium rejection is found, at \( 10^{-4} \) mol/l \( KCl \) it is up to 82%. For UFM-100 membrane the maximum potassium rejections reaches 37 % at \( 10^{-4} \) mol/l and 47 % at \( 10^{-5} \) mol/l. Potassium rejection can be explained by the following mechanism: the membrane surface inside the pores is negatively charged due to dissociation of acetate groups on the membrane surface. This causes cations to be attracted towards the surface leading to accumulating a positive charge inside the pores; this process results in electric repulsion of the cations approaching a pore called a negative adsorption. The later leads two membrane surface of a pore placed at such a small distance that the boundary layers of the surfaces overlap and the average concentration of dissolved substance in the pore is less than the concentration in the bulk solution. In case of UFM-200 membrane the maximum potassium rejections get to 30% at \( 10^{-4} \) mol/l and 37% at \( 10^{-5} \) mol/l. However for UFM-200 membrane the rejection coefficient decreases more sharply. The effect of the rejection coefficient decreasing can be explained by a sieving mechanism, when a radius of the hydrated ion is equal or less than the radius of the membrane pore (Starov and Churaev 1993).
Fig. 5.13 Rejection coefficient of KCl via filtration velocity for UFM-50 membrane.
Fig. 5.14 Rejection coefficient of KCl via filtration velocity for UFM-100 membrane.

Fig. 5.15 Rejection coefficient of KCl via filtration velocity for UFM-200 membrane.
Fig. 5.16 $f$ as function of filtration velocity for UFM-50 membrane.

Fig. 5.17 $f$ as function of filtration velocity for UFM-100 membrane.
Fig. 5.18 $f$ as function of filtration velocity for UFM-200 membrane.

Fig. 5.19 $f$ as function of filtration velocity of KNO$_3$ and K$_2$SO$_4$ for UFM-100 membrane.
In Fig. 5.19 experimental data of $\text{KNO}_3$ and $\text{K}_2\text{SO}_4$ with concentration $10^{-4}$ mol/l for UFM-100 membrane are presented as $f$ function via filtration velocities. For $\text{K}_2\text{SO}_4$ solution, when the sign of the more charged $\text{SO}_4^{2-}$ ions coincide with the negative charge of the membrane, the rejection is higher than for $\text{KNO}_3$ and even higher than for $\text{KCl}$ (Fig. 5.17). The repulsion forces of bivalent ions by the membrane surface are stronger than monovalent ions (Starov and Churaev, 1993).

These experimental results show interactions between the dissolved ions and the membrane surface, which lead to decrease or increase of positive rejection of these ions by the membrane.

5.5 Conclusion

A new theoretical method to determine the polyelectrolyte charge through diffusion coefficient values has been developed and validated against experimental data. The percentage of dissociated sites of the polyelectrolyte has been calculated and plotted against the polyelectrolyte concentration. The theoretical values are in good agreement with the data obtained here. Furthermore a technique for the determination of diffusion coefficient using conductivity measurements has been proposed and successfully employed. Moreover the diffusion coefficient of NaPSS estimated through conductivity measurements is of the same order of the value found in literature obtained through photon correlation spectroscopy.
CHAPTER 6: CONCENTRATION OF INORGANIC SALTS IN THE PERMEATE PROMOTED BY A POLYELECTROLYTE DURING ULTRAFILTRATION

6.1 Introduction

In this chapter the theoretical approach developed previously (see Chapter 4) will be initially validated against data obtained from literature using mixtures of different salts such as NaCl, KCl and RbCl with a cationic polyelectrolyte (PDDA, MW 35 kDa). As the fitting proved satisfactory, other experimental data produced for this work (using CsCl, MgCl₂, K₂SO₄, KCl and KNO₃) with the same polyelectrolyte (PDDA, MW 137 kDa) will be used to check if the method suggested is valid for salts with different cations. The tested solutions were single salts or mixtures of two salts with mono- and divalent ions with added PDDA at various concentrations.

The concentration of anions (boron ions) in the permeate stream, using a cationic polyelectrolyte dissolved in the feed solution, has been successfully achieved. In order to do this a different polyelectrolyte (NaPSS, MW 200 kDa) was selected; the theory developed will be validated also in this case against filtration results of different boron solutions at various concentrations of boron and polyelectrolyte. Also the influence of pH and the presence of other ions in the solution were investigated.
6.2 Concentration of potassium and cesium in the permeate in the presence of the cationic polyelectrolyte PDDA

Theoretical predictions based on equation (4.74) were compared with experimental data. The first three sets for comparison were taken from (Starov et al., 1996), where ultrafiltration experimental data of KCl, NaCl, RbCl in the presence of PDDA are presented. The molecular weights of the polyelectrolyte and the monomer unit used there were 35 kDa and 161, respectively. The number of dissociable units (N=35,000/161≈217) is substantially smaller than in the experiments presented later in this chapter. The degree of metal concentration in the permeate solution of KCl, NaCl, RbCl reported in (Starov et al., 1996) was compared with the theory deduced in this study (Equation (4.74)). Comparison of the experimental data (symbols) with the model predictions (solid line) is presented in Fig. 6.1, Fig. 6.2 and Fig. 6.3. In all cases under consideration, inorganic salts were not rejected by the membrane (averaged membrane pore size was more than 15 nm), consequently \( \gamma = 1 \) was set in equation (4.74) in accordance with this observation. The model parameters are listed in the Appendix III. As can be seen from these figures, the agreement between the experimental data and the model proposed is good for the condition when the membrane does not offer any rejection of inorganic cations from the permeate.
Fig. 6.1 Concentration of KCl solutions in the permeate: experimental data and model prediction from equation (4.74).

Fig. 6.2 Concentration of NaCl solutions in the permeate: experimental data and model prediction from equation (4.74).
Fig. 6.3 Concentration of RbCl solutions in the permeate: experimental data and model prediction from equation (4.74).

As the preliminary validation of the theory proved satisfactory, other experimental conditions such as a membrane pore size and other inorganic salts and their mixtures with the polyelectrolyte were investigated. Filtration results were collected and compared with the model predictions.

First, the effect of the polyelectrolyte concentration on the filtration velocity (using UFM-100) was performed and the results are in Fig. 6.4. When ultra pure water was filtered the relation between applied pressure and filtration velocity is linear. The addition of 0.1 g/l PDDA does not change the behaviour. The experimental points are in the same line with ultra pure water up to 3.0 bar, above that, a decrease of filtration velocity is noticeable, indicating a gel layer formation (see 2.1.2) due to increase of PDDA concentration in vicinity of the membrane surface. Further addition of PDDA (0.4 and 0.8 g/l) leads to the appearance of plateau above 2.5 bar and these curves are remarkably lower than the values of ultra pure water.
Fig. 6.4 Filtration velocity versus applied pressure for UFM-100.

Fig. 6.5 and Fig. 6.6 show potassium concentration in the permeate versus filtration velocity for UFM-100. These experimental results were compared with the theory predictions (Eq. 4.74) and the model data is presented in the Appendix IV. In Fig. 6.5 experimental results for mixtures of KCI of $10^{-4}$ mol/l and 0.2, 0.3 and 0.4 g/l PDDA are presented. At low filtration velocity potassium concentration is high and decreasing down to the minimum with filtration velocity increase. The decrease of $\Lambda$ at high filtration velocities is explained by the gel layer formation. The sign of a gel layer formation has been shown earlier in Fig. 6.4. Addition of PDDA gives an increase of potassium concentration in the permeate which is consistent with the model developed (see Chapter 4). However in Fig. 6.6 an opposite effect is noticed. Addition of PDDA from 0.5 g/l to 1.0 g/l decreases potassium concentration in the permeate. This is due to a gel layer formation at high PDDA concentrations. Extrapolation of $\Lambda$ to the zero filtration velocity provides the maximum values of $\Lambda$. The effect of PDDA concentration on $\Lambda_0$ is shown in Fig. 6.7. At low PDDA concentration $\Lambda$ is increasing, it means that the potassium concentration in the permeate is increasing with respect to PDDA concentration in the feed solution. However, this curve reaches a peak at
approximately 0.5 g/l PDDA where \( \Lambda_0 \) is 3.5 and declines further as a result of a gel layer formation.

Cesium concentration in the permeate versus filtration velocity for the mixture of \( \text{CsCl} \) with concentration in order of \( 10^{-4} \) mol/l and 0.5; 0.8; 1.0 g/l of PDDA for UFM-100 is presented in Fig. 6.8. In the case of \( \text{CsCl} \), as in the case of \( \text{KCl} \), a degree of metal concentration in the permeate is very high, in some cases is up to 2.5-3.0 at small filtration velocities and steadily reduced with increasing filtration velocity.

Fig. 6.5 Potassium concentration in the permeate versus filtration velocity for the mixture of \( \text{KCl} \) of \( 10^{-4} \) mol/l and 0.2; 0.3; 0.4 g/l PDDA concentrations for UFM-100: experimental data and model prediction from equation (4.74).
Fig. 6.6 Potassium concentration in the permeate versus filtration velocity for the mixture of KCl of $10^{-4}$ mol/l and different concentrations of PDDA for UFM-100: experimental data and model prediction from equation (4.74)

Fig. 6.7 Potassium concentration in the permeate at zero filtration velocity (extrapolated) as a function of PDDA concentration for the mixture of KCl of $10^{-4}$ mol/l and different concentrations of PDDA for UFM-100.
Fig. 6.8 Cesium concentration in the permeate versus filtration velocity for the mixture of CsCl with concentration of $10^{-4}$ mol/l and 0.5; 0.8; 1.0 g/l of PDDA for UFM-100: experimental data and model prediction from equation (4.74).

In Fig. 6.9 and Fig. 6.10 ultrafiltration data are presented for mixtures of 0.5 g/l PDDA and KCl $1 \times 10^{-5}$ mol/l or CsCl $1 \times 10^{-5}$ mol/l correspondingly. In both cases high values of degree of metal concentration in the permeate are detected at low filtration velocities. At zero velocities $\Lambda$ reaches up to 6.0.
Fig. 6.9 Potassium concentration in the permeate versus filtration velocity for the mixture of KCl \(1.02 \times 10^{-5}\) mol/l and 0.5 g/l of PDDA for UFM-100: experimental data and model prediction from equation (4.74).

Fig. 6.10 Cesium concentration in the permeate versus filtration velocity for the mixture of CsCl \(1.0 \times 10^{-5}\) mol/l and 0.5 g/l of PDDA for UFM-100: experimental data and model prediction from equation (4.74)
Different inorganic salts of the same concentration $10^{-4} \text{ mol/l}$ such as $\text{KCl}$, $\text{KNO}_3$, $\text{K}_2\text{SO}_4$ were used in the presence of $\text{PDDA}$ of concentration $0.5 \text{ g/l}$ during ultrafiltration. It was found that, in case of $\text{KCl}$, potassium concentration in the permeate is much higher than in cases of $\text{KNO}_3$ or $\text{K}_2\text{SO}_4$. Rejection coefficient of potassium is becoming less negative in the presence of potassium nitrate, and even less negative in the case of potassium sulphate. In Fig. 6.11 potassium concentration in the permeate versus filtration velocity for the mixture of different salts with concentrations in order of $10^{-4} \text{ mol/l}$ and $0.5 \text{ g/l}$ of $\text{PDDA}$ for UFM-100 is shown. The explanation of the phenomena can be as follows: ion with higher surface charge replaces chloride ion $(\text{Cl}^-)$ in the polymer. From the literature (Nightingale, 1959) the radius of chloride ion is $0.181 \text{ nm}$, the crystal radius of nitrate ion is $0.264 \text{ nm}$, the crystal radius of sulphate ion is $0.290 \text{ nm}$. It is known that a localized negative charge such as that of $\text{Cl}^-$ rather than a delocalized charge as in the case of nitrate $(\text{NO}_3^-)$, sulphate $(\text{SO}_4^{2-})$, is essential for maximal activation. Taking into account the above information the substitution ability of the inorganic ions into $\text{PDDA}$ is following: $\text{Cl}^- < \text{NO}_3^- < \text{SO}_4^{2-}$. As a result less nitrate and sulphate anions can go through the membrane due to their complex formation with the polyelectrolyte molecules.

Moreover the hydrated size of ions has an effect on ion mobility and diffusivity, thus affecting the permeation in UF processes. As can be observed from Table 6.1, $\text{SO}_4^{2-}$ has the lowest mobility compared with $\text{NO}_3^-$ and $\text{Cl}^-$ ions. $\text{Cl}^-$ has a considerably higher mobility than other anions.
Table 6.1 Diffusion coefficients, conductivity and mobility of certain ions in water at infinitive dilution at a temperature of 25°C (Lide and Kehialan, 1994).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Diffusion coefficient $[10^{-9} \text{ m}^2 \text{ s}^{-1}]$</th>
<th>Specific conductivity $[10^{-4} \text{ m}^2 \text{ S mol}^{-1}]$</th>
<th>Mobility $[10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cl^-$</td>
<td>2.032</td>
<td>76.3</td>
<td>7.9</td>
</tr>
<tr>
<td>$NO_3^-$</td>
<td>1.902</td>
<td>71.4</td>
<td>7.4</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>1.065</td>
<td>40.0</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Fig. 6.11 Potassium concentration in the permeate versus filtration velocity for the mixture of different salts with concentrations of $10^{-4}$ mol/l and 0.5 g/l of PDDA for UF-100: experimental data and model prediction from equation (4.74).
In Fig. 6.12 filtration velocity versus applied pressure is presented for UFM-200. At 0.5 g/l of PDDA filtration velocity is proportional to the applied pressure and has a linear character. Addition of more PDDA changes the situation and at 0.8 g/l of PDDA at low pressure it is linear followed by a plateau corresponding to 28 μm/s.

In Fig. 6.13 potassium concentration in the permeate versus filtration velocity for the mixture of KCl of 10^{-4} mol/l with 0.5; 0.8 and 1.36 g/l PDDA concentrations for UFM-200 is shown. In all cases significant concentration of potassium in the permeate is observed at relatively low filtration velocity. A is maximum at zero filtration velocity and steadily decreases until it reaches a constant value at 10 μm/s. With increase concentration of PDDA A increases accordingly adding 0.5 g/l and 0.8 g/l. This behaviour is in good agreement with the theory. However further addition of PDDA leads to decrease of A as in the case of 1.36 g/l. In Fig. 6.14 potassium concentration in the permeate versus filtration velocity for the mixture of KCl in order of 10^{-5} mol/l
and 0.5; 1.0 g/l PDDA concentrations for UFM-200 is shown. In both cases significant potassium concentration in the permeate is observed.

Fig. 6.13 Potassium concentration in the permeate versus filtration velocity for the mixture of KCl of $10^{-4}$ mol/l and 0.5; 0.8; 1.36 g/l PDDA concentrations for UFM-200: experimental data and model prediction from equation (4.74).
Fig. 6.14 Potassium concentration in the permeate versus filtration velocity for the mixture of KCl of $10^{-5}$ mol/l and 0.5; 1.0 g/l PDDA concentrations for UFM-200: experimental data and model prediction from equation (4.74).

In Fig. 6.15 filtration velocity versus applied pressure is shown for UFM-100 for $K_2SO_4$ solutions. Discrepancies between the dependence of filtration velocity against applied pressure of pure water and mixtures $K_2SO_4$ with PDDA are noticeable above 2.0 bar where the solution $K_2SO_4$-PDDA tends to have a plateau character instead of the linear profile exhibited by the pure water.

Potassium concentration in the permeate versus filtration velocity for the mixture of $K_2SO_4$ of $10^{-4}$ mol/l and 0.5 g/l or 0.8 g/l PDDA concentrations for UFM-100 is presented in Fig. 6.16. In both cases significant concentration of potassium in the permeate is observed at filtration velocity up to 3.0 $\mu$m/s, further it decreased to its minimum. Potassium concentration in the permeate versus filtration velocity for the mixture of $K_2SO_4$ in order of $10^{-6}$ mol/l and 0.5 g/l or 0.8 g/l PDDA concentrations for
UFM-100 is shown in Fig. 6.17. In case of 0.8 g/l of PDDA, $\Lambda > 1$ tends to be only at a very low filtration velocity, at 5.0 $\mu$m/s it reaches its minimum equal 1.

In Fig. 6.16 and Fig. 6.17 the degree of potassium concentration is higher at 0.5 g/l of PDDA compared with 0.8 g/l and it is higher at more diluted salt solutions, it is higher at $10^{-5}$ mol/l of $K_2SO_4$ than at $10^{-4}$ mol/l of $K_2SO_4$.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{filtration_velocity_graph}
\caption{Filtration velocity versus applied pressure for UFM-100.}
\end{figure}
Fig. 6.16 Potassium concentration in the permeate versus filtration velocity for the mixture of $K_2SO_4$ in order of $10^{-4}$ mol/l and 0.5 g/l and 0.8 g/l PDDA concentrations for UFM-100: experimental data and model prediction from equation (4.74).

Fig. 6.17 Potassium concentration in the permeate versus filtration velocity for the mixture of $K_2SO_4$ in order of $10^{-5}$ mol/l and 0.5 g/l and 0.8 g/l PDDA concentrations for UFM-100: experimental data and model prediction from equation (4.74).
In Fig. 6.18 filtration velocity as a function of applied pressure for UFM-200 is presented for water and mixtures of \( K_2SO_4 \) with PDDA. In Fig. 6.19 potassium concentration in the permeate versus filtration velocity for the mixture of \( K_2SO_4 \) in order of \( 10^{-4} \) mol/l and 0.5 g/l and 1.0 g/l of PDDA for UFM-200. In both cases \( \Lambda \) is high at low filtration velocities and decreases with increase of filtration velocity during ultrafiltration.

Fig. 6.18 Filtration velocity versus applied pressure for UFM-200.
Fig. 6.19 Potassium concentration in the permeate versus filtration velocity for the mixture of $K_2SO_4$ in order of $10^{-4}$ mol/l and 0.5 g/l and 1.0 g/l of PDDA for UFM-200: experimental data and model prediction from equation (4.74).

Fig. 6.20 Rejection of magnesium as a function of filtration velocity for the UFM-100.
Fig. 6.20 shows the rejection of magnesium versus filtration velocity with various feed PDDA concentrations and without for UFM-100 membrane. Pure solution of $10^{-4}$ mol/l $\text{MgCl}_2$ exhibits 89-95% of magnesium rejection. Addition of 0.3 g/l PDDA does not have any effect on magnesium rejection. However, adding 0.5 g/l PDDA decreases magnesium rejection dramatically down to 0.09 at filtration velocity of 3.84 $\mu$m/s. At low filtration velocity magnesium rejection is very low and increased with increasing filtration velocity and, consequently, with the appearance of a gel layer polarization due to increasing concentration of PDDA near the membrane surface.

With higher concentration of PDDA, 0.6 g/l, a gel layer formation takes place immediately and prevents the decrease of magnesium chloride concentration towards negative rejection values through concentration of its cations in the permeate.

Experiments with mixtures of $\text{MgCl}_2$ and different concentrations of PDDA showed a tendency to concentration of magnesium in the permeate due to PDDA presence compared with pure $\text{MgCl}_2$ solution. Nevertheless 0.5 g/l of PDDA appeared not to be enough to concentrate magnesium in the permeate and 0.6 g/l of PDDA was high enough to create a gel layer.

![Rejection of magnesium as a function of filtration velocity for the UFM-200.](image)

Fig. 6.21 Rejection of magnesium as a function of filtration velocity for the UFM-200.
Filtration data for UFM-200 for mixtures of $10^{-4}$ mol/l MgCl$_2$ and different concentrations of PDDA is shown in Fig. 6.21. The same tendency as in Fig. 6.20 is observed. Addition of PDDA up to 0.5 g/l decreases magnesium rejection to 0.15 at low filtration velocities. However this PDDA concentration is not sufficient to give a negative magnesium rejection.

![Fig. 6.22 Rejection of magnesium as a function of filtration velocity for the UFM-200](image)

In Fig. 6.22 rejection of magnesium versus filtration velocities is compared for pure MgCl$_2$ of $10^{-5}$ mol/l and a mixture of $10^{-5}$ mol/l MgCl$_2$ with 0.8 g/l PDDA. It is clear from the graph that magnesium is rejected less by the membrane in the presence of the polyelectrolyte, especially at a low filtration velocity ($R = 0.38$ at 7.44 mm/s). It is suggested that the polyelectrolyte has its influence on the transport of magnesium through the membrane, however in this case the influence of the polyelectrolyte is not strong enough to lead to magnesium concentration in the permeate stream.
Fig. 6.23 Rejection of magnesium and potassium as a function of filtration velocity for the mixture of KCl $10^{-4}$ mol/l + MgCl$_2$ $5 \times 10^{-5}$ mol/l + 0.8 g/l PDDA for the UFM-200.

Fig. 6.23 shows experimental data for potassium and magnesium rejections versus filtration velocity for UFM-200. The experimental data has the following features: magnesium rejection is constant up to the filtration velocity 27.8 µm/s. Further increase of filtration velocity leads to rapid decrease of magnesium rejection from 0.55 to 0.2. As for potassium rejection initially it is increasing slowly from negative values to the small positive values, from -0.2 to 0.1. At higher filtration velocity potassium rejection does not longer depend on filtration velocity. At filtration velocity 14.8 mm/s potassium rejection as a function of filtration velocity has a plateau character.
Fig. 6.24 Rejection of magnesium and potassium as a function of filtration velocity for the mixture of KCl $10^{-4}$ mol/l + MgCl$_2$ $10^{-4}$ mol/l + 0.8 g/l PDDA for the UFM-200.

Analogical filtration data as in Fig. 6.23 is presented in Fig. 6.24, Fig. 6.25 and Fig. 6.26 for UFM-200. In Fig. 6.24 experimental data for mixtures of KCl $10^{-4}$ mol/l with MgCl$_2$ $10^{-4}$ mol/l and 0.8 g/l PDDA is shown. Magnesium rejection remains constant during the filtration process with a small decrease at high filtration velocities. Potassium rejection is negative at low filtration velocities up to 20.0 μm/s with increase into positive rejection up to 0.2. In Fig. 6.25 and Fig. 6.26 the behaviour of potassium rejection is similar to Fig. 6.24. In Fig. 6.25 magnesium rejection is constant at low filtration velocities with slow decrease with filtration velocity increasing. In Fig. 6.26 magnesium rejection is decreasing slowly in the beginning and more sharply to the end.
Fig. 6.25 Rejection of magnesium and potassium as a function of filtration velocity for the mixture of $\text{KCl} \ 10^4 \text{ mol/l} + \text{MgCl}_2 \ 5\times 10^4 \text{ mol/l} + 0.8 \text{ g/l PDDA}$ for the UFM-200.

Fig. 6.26 Rejection of magnesium and potassium as a function of filtration velocity for the mixture of $\text{KCl} \ 10^4 \text{ mol/l} + \text{MgCl}_2 \ 10^{-3} \text{ mol/l} + 0.8 \text{ g/l PDDA}$ for the UFM-200.
Ultrafiltration experimental results and theoretical curves for mixtures of KCl $10^{-4}$ mol/l, 0.8 g/l PDDA and different concentrations of MgCl₂ are presented in Fig. 6.27. Concentration of potassium in the permeate as a function of feed MgCl₂ concentration for the UFM-200 membrane at 0.6 bar is shown in Fig. 6.27. MgCl₂ concentration in the feed solution was varied from $5 \times 10^{-5}$ mol/l till $10^{-3}$ mol/l. Comparison of potassium rejection alone and in the presence of MgCl₂ shows that even a small presence of MgCl₂ ($5 \times 10^{-5}$ mol/l) gives an increase of potassium concentration in the permeate from $\Lambda = 1.1$ (without presence of MgCl₂) up to $\Lambda = 1.21$. Further increase of potassium concentration in the permeate is a result of larger feed concentration of MgCl₂. Concentration of potassium is reached its maximum $\Lambda = 1.41$ in the presence of $5 \times 10^{-4}$ mol/l of MgCl₂ in the feed solution. Addition of more MgCl₂ ($10^{-3}$ mol/l) leads to a decrease concentration of potassium in the permeate which can be explained that MgCl₂ does not dissociate completely at such high concentration and consequently does not release enough chloride ions in the feed solution to promote an increase of potassium permeation through the membrane.
The model predicted the experimental data only at low filtration velocity (where no gel layer formation occurred), in this region the model over estimated the ion rejection because of the assumption that a pure salt is not rejected by the membrane, which means $\Lambda = 1$.

\[ \begin{array}{c}
\text{MgCl}_2 \text{ concentration (mol/l)} \\
0 \quad 5.00E-05 \quad 1.00E-04 \quad 5.00E-04 \quad 1.00E-03
\end{array} \]

\[ \begin{array}{c}
\Lambda \text{ (potassium)} \\
0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \quad 1.2 \quad 1.4 \quad 1.6
\end{array} \]

\textbf{Fig. 6.28 Potassium concentration in the permeate (initial concentration of KCl $10^{-4}$ mol/l, PDDA concentration 0.8 g/l) as a function of feed MgCl}_2 \text{ concentrations for the UFM-200 membrane at 0.6 bar.}

This fact can be explained by the relatively high MgCl$_2$ concentration (more than $5\times10^{-4}$ mol/l) at which MgCl$_2$ was not fully dissociated. It is known from literature [Freger et al., 2000; Nyström et al., 1995] that the most distinct effect of Donnan equilibrium is reached when salts are fully dissociated. The level of dissociation can be linked to the Donnan equilibrium effect on ion separation. A decrease in dissociation possibly decreases the effect of Donnan potential on ion separation.
separation: the effect of retained species concentration on permeable species is decreased.

6.3 Concentration of boron in the permeate in the presence of the anionic polyelectrolyte in the feed solution

Fig. 6.29 shows the dependence of the average water flux through the membrane against applied pressure. Data shown represent the average and standard deviation of five independent experiments; water permeability calculated from the experimental data was 7.82 μm/s bar. As can be seen the dependence of the water flux against applied pressure has a linear character. In Fig. 6.30 a linear dependence between filtration velocity and applied pressure is observed for 0.4 ppm of boron and for its mixture with 1.0 g/l NaPSS at pressures up to 1.5 bar, above a deviation from the linearity is evident in the case of boron mixture with NaPSS. However this deviation does not exceed 15%. Increasing the boron concentration to 1 ppm does not affect the filtration velocity of pure solution (Fig. 6.31) whilst when 1.0 g/l of NaPSS is added the filtration velocity deviates from linearity above 1 bar. In Fig. 6.32 filtration velocity as a function of applied pressure is shown for mixtures of 2 ppm of boron and different concentrations of NaPSS. The presence of the polyelectrolyte reduces the filtration velocity, moreover this effect is increasing with increasing NaPSS concentrations.

![Graph showing water flux versus working pressure](image)

**Fig. 6.29. Water flux versus working pressure**
Fig. 6.30 Filtration velocity as a function of applied pressure for UFM-100

Fig. 6.31 Filtration velocity as a function of applied pressure for UFM-100
Fig. 6.32 Filtration velocity as a function of applied pressure for UFM-100

Comparison of boron concentration in the permeate versus applied pressure with fixed polyelectrolyte concentration (1.0 g/l) and different boron concentrations in the feed solution in the range of pH = 5.98-9.25 is presented in Fig. 6.33. In all cases some negative boron rejection was observed. Boron showed less negative rejection than was observed in the case of other inorganic salts, such as KCl, CsCl. This can be explained by complicated boron chemistry, as boron in aqueous solutions exists in different ion forms depending on pH (see Fig. 2.3 in Chapter 2). Also boron, due to its chemical structure, tends to interact in the aqueous solutions forming complexes by donor-acceptor interactions. Extrapolating $\Lambda$ at zero filtration velocity the following $\Lambda_0$ parameters were found from Fig. 6.33: 1.70 (for 0.4 ppm B+1.0 g/l NaPSS); 1.50 (for 1.0 ppm B+1.0 g/l NaPSS); 1.38 (for 2.0 ppm B+1.0 g/l NaPSS). Experimental data were fitted according to the equation 4.74 in Chapter 4, which shows good prediction with experimental data. Thickness of a laminar boundary layer was used as a fitting parameter (see Appendix V).
Fig. 6.33 Dependence $\Delta$ from filtration velocities for different boron concentrations at fixed feed NaPSS concentration (1.0 g/l): experimental data and model prediction from equation (4.74)).

Fig. 6.34 Comparison of boron concentration in the permeate at 0.4 bar with fixed polyelectrolyte concentration (1.0 g/l) and feed boron concentration (0.4 ppm) in the presence of different inorganic salts of 0.04 mol/l at pH 5.82-6.32.
It should be noticed that even at pH = 5.98 - 6.4 (Fig. 6.33) when boron mainly exists in the form of a pure boric acid (Chapter 2, Fig. 2.3) a significant boron concentration in the permeate is observed, which is in agreement with the existence of boron in the anionic form in aqueous solutions at this pH range.

Comparison of boron concentration in the permeate at 0.4 bar with fixed polyelectrolyte concentration (1.0 g/l) and feed boron concentration (0.4 ppm) in the presence of different inorganic salts at concentration equal to 0.0187 mol/l at pH ranging between 5.82 and 6.32 is presented in Fig. 6.34. It is shown that in the presence of other ions such as $SO_4^{2-}$, $NO_3^-$, boron concentration in the permeate increased and boron negative rejection decreased accordingly. It means that these ions promoted boron concentration in the permeate. However in case of presence of $Cl^-$ ions the opposite effect was observed. Positive boron rejection was observed so boron was not concentrated in the permeate solution as result of the competition between $Cl^-$ and boron species in the feed solution during filtration process, $Cl^-$ ions due to their small size and mobility were able to go through the membrane and compensate the neutrality balance instead of boron anions. That is why boron is partially rejected by the membrane. This results suggest that ions with bigger sizes, such as $SO_4^{2-}$ and $NO_3^-$ can cross the membrane with more difficulty than the boron, consequently the boron concentration in the permeate increases to keep the charge balance.
In Fig. 6.35 degree of boron concentration versus filtration velocity is shown for 2 ppm of boron solution in the presence of 0.5 g/l and 1.0 g/l NaPSS and 0.01 mol/l NaHCO₃.

In both cases significant concentration of boron in the permeate are observed at low filtration velocity and the degree of boron concentration was decreasing with an increase of filtration velocity. Apparently the degree of boron concentration is higher at 0.5 g/l NaPSS than at 1.0 g/l of NaPSS, which is in the contradiction with the theory presented in Chapter 4. However this phenomenon can be explained by the appearance of a gel layer formation at 1.0 g/l even at low filtration velocities leading to the reduction of the degree of boron concentration in the permeate. Moreover at filtration velocities above 8 μm/s boron is retained by the membrane, it is assumed that this fact is due to a gel layer formation of NaPSS on the membrane surface in case of using 1.0 g/l of the polyelectrolyte.
Fig. 6.36 Boron concentration in the permeate at 0.4 bar versus different NaPSS concentration at pH 9.20-9.32.

In Fig. 6.36 filtration data of mixtures 2.0 ppm boron with NaPSS of different concentrations and pH ranged from 9.20 to 9.32 at 0.4 bar are presented. 0.4 bar has been selected as at this pressure the maximum experimentally available $\Lambda$ values were obtained. As can be seen in Fig. 6.36 maximum boron concentration in the permeate is observed at 0.5 g/l of NaPSS. Increasing of the polyelectrolyte concentration leads to the decreasing of $\Lambda$. At 2.0 g/l of NaPSS boron is rejected by the membrane, a degree of boron concentration is less than 1. This effect is due to a gel layer formation on the membrane surface.
6.4 Conclusions

It has been demonstrated that it is possible to concentrate cations within the permeate stream from an ultrafilter by using a polyelectrolyte in aqueous solutions. The degree of concentration in the permeate, compared to the remaining concentration in the feed, is several times — in some cases as high as 400%. The polymer remains retained by the membrane filter and can be reused within the process. A new modelling analysis has been presented and validated against previously published experimental work, where the membrane was sufficiently open that it had no inherent rejection capability for the cations under investigation. The agreement between the model and the data was very good. In this experimental work, performed also with a finer pored membrane which had a significant ability to reject cations, the concentration of cations in the permeate was still observed — despite the inherent ability of the membrane to reject the ions. The model was fitted with the assumption of no rejection of pure salts, this was not strictly correct for the smallest pores, however the model prediction proved satisfactory even in the later case.

The filtration process was performed on solutions of different salts and their mixtures. The concentration of monovalent ions in the permeate stream such as potassium, cesium, rubidium, sodium appeared easier than bivalent ions such as magnesium. The higher difficulty of this ion to cross the membrane would require higher polyelectrolyte concentration, however the gel layer formation occurred before a negative magnesium rejection was achieved. Nevertheless, at low PDDA concentration the rejection of magnesium in the permeate was lower than without the polyelectrolyte supporting the theory that the polyelectrolyte dissociation facilitates the transfer through the membrane of these ions.

The attempt to concentrate anions using an anionic polyelectrolyte (NaPSS) was investigated for boron solutions (boric acid and sodium borates). Results showed the importance of the pH values and the presence of other ions in the solution. Initial results suggest that the approach is feasible and the theoretical description of the process is correct.
7.1 Conclusions

The feasibility to concentrate inorganic low-molecular weight components in the permeate stream of ultrafiltration membranes employing a polyelectrolyte in the feed solution has been successfully shown. The membrane used was able to completely retain the polyelectrolyte that can be reused for the process. The described method is an innovative development of the already established Nano-/Ultrafiltration. The enhanced efficiency of recovery is particularly interesting for low pressure and small filtrate volume are produced. Both factors result in reduced operational cost compared with Reverse Osmosis. Moreover, it has been shown that the best results are achieved when salts are very diluted. This makes the process highly appealing for the treatment of solutions which present low concentration ions needing recovery.

The diffusion coefficient of a polyelectrolyte and the polyelectrolyte charge have been successfully determined by a new theoretical method based on conductivity measurement. The theoretical predictions are in good agreement with the data obtained here. Moreover, the diffusion coefficient of NaPSS estimated through conductivity measurements is of the same order of the value obtained through photon correlation spectroscopy. Furthermore, model parameters such as a, b and g have been independently obtained from experimental data. Hence, the modelling approach has been demonstrated to be truly predictive.
7.2 Recommendations for future work

The aim of this work was to show that it is possible to concentrate inorganic salts in the permeate adding a polyelectrolyte in the feed solution during Ultrafiltration processes. It has been verified that monovalent metals such as potassium, sodium, rubidium, cesium can be concentrated in the permeate stream during ultrafiltration. However, it has not been possible to concentrate bivalent metals such as magnesium. In order to do this, it is suggested to use the similar membranes with bigger pore size.

The work in this thesis has been performed using only cellulose acetate membranes rated at 5 to 15 nm. Cellulose acetate membranes have several limitations such as temperature, oxidant resistant and pH operating range (pH = 3 - 8). In industrial applications ceramic membranes are becoming widely used nowadays. Ceramic membranes (Al₂O₃, TiO₂, ZrO₂) are versatile and combine the advantages of their high chemical, mechanical and thermal resistance. Their high temperature resistance and wide pH-range are important for the cleaning/sterilization in the Bio/Pharma- and Food industries. Moreover ceramic membranes are oxidant resistant and have a long operating life. All this makes ceramic membranes very attractive for use in industry. Consequently, for the purpose of industrial use, this work needs to be repeated at the same range of membranes pore size using ceramic membranes. Also for experiments with boron solutions it would be advantageous to use membranes with a wider pH operating range, as it is known that boron predominantly exists in an anionic form in alkaline solutions. Polysulfonate membranes would be suitable for this purpose as they are relatively cheap and have pH working range from 2 to 12.

The filtration experiments have been conducted using one type of cationic polyelectrolyte (in case of potassium and cesium concentration) and one type of anionic polyelectrolyte (in case of boron concentration). It would be interesting to use several different polyelectrolytes with different structures to show the influence of
polyelectrolyte nature on the effect of salt concentration in the permeate during ultrafiltration.

All filtration experiments have been performed using a stirred filtration cell. However cross-flow filtration is more applicable for industrial processes as several problems common during dead-end filtration, such as flux decline due to concentration polarization and fouling problems, requiring frequent cleaning or change out of filters can be avoided. This work could be extended to scale-up the process using a modular cross-flow rig and optimizing working conditions such as temperature, pH, applied pressure and flow rate. Also, it would be advisable to use not only pure mixtures of salt solutions with a polyelectrolyte, but also apply the developed method to waste water treatment.

A new membrane separation method by inorganic salts concentration in the permeate in the presence of a polyelectrolyte in the feed solution during ultrafiltration has been proposed, investigated and modelled. However, to scale up and implement the process in industry the above recommendations should be followed.
## APPENDIX I

<table>
<thead>
<tr>
<th>pore number</th>
<th>UFM-50 pore size (nm)</th>
<th>UFM-100 pore size (nm)</th>
<th>UFM-200 pore size (nm)</th>
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</thead>
<tbody>
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<td>12.9</td>
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<td>25</td>
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<td>10.4</td>
<td>16.8</td>
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<table>
<thead>
<tr>
<th></th>
<th>UFM-50</th>
<th>UFM-100</th>
<th>UFM-200</th>
</tr>
</thead>
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<td>average pore size (nm)</td>
<td>6.3</td>
<td>9.6</td>
<td>15.1</td>
</tr>
<tr>
<td>standard deviation</td>
<td>1.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>porosity (%)</td>
<td>59</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>
Taking into account that \( \frac{\alpha N}{1 + \alpha} \) we can rewrite the equation (4.18) as:

\[
\frac{\alpha N}{1 + \alpha} = \frac{\alpha^0}{\alpha} - \lambda,
\]

Multiplying both sides of the latter equation \((1 + \alpha)\alpha\) we can get:

\[
\alpha^2 N = \alpha^0 (1 + \alpha) - \lambda \alpha (1 + \alpha),
\]

\[
\alpha^2 N = \alpha^0 + \alpha^0 \alpha - \lambda \alpha - \lambda \alpha^2,
\]

\[
\alpha^2 (N + \lambda) + (\lambda - \alpha^0) \alpha - \alpha^0 = 0.
\]

Assuming that \( \alpha > 0 \):

\[
\alpha = \frac{-(\lambda^0 - \alpha^0) \pm \sqrt{(\lambda^0 - \alpha^0)^2 + 4\alpha^0 (N + \lambda)}}{2(N + \lambda)},
\]

\[
(\lambda^2 - \alpha^0)^2 + 4\alpha^0 N + 4\alpha^0 \lambda = \lambda^2 - 2\lambda \alpha^0 + \alpha^0 + 4\alpha^0 N + 4\alpha^0 \lambda =
\]

\[
= \lambda^2 + 2\lambda \alpha^0 + \alpha^0 + 4\alpha^0 N = (\lambda + \alpha^0)^2 + 4\alpha^0 N > 0
\]

\[
\alpha = \frac{-(\lambda^0 - \alpha^0) \pm \sqrt{(\lambda^0 + \alpha^0)^2 + 4\alpha^0 N}}{2(N + \lambda)},
\]

as \( \sqrt{(\lambda + \alpha^0)^2 + 4\alpha^0 N} > \lambda + \alpha^0 \) we can arrive to the following equation:
\[
\alpha = \frac{-(\lambda - \alpha^0) + \sqrt{(\lambda + \alpha^0)^2 + 4\alpha^0 N}}{2(N + \lambda)},
\]

\[
\frac{\alpha N}{1 + \alpha} = \frac{(\alpha + 1 - 1)N}{1 + \alpha} = \frac{N(1 + \alpha)}{1 + \alpha} = \frac{N(1 - \frac{1}{1+\alpha})}{1+\alpha}.
\]

Multiplying a numerator and a denominator on \(\frac{(2N + \lambda + \alpha^0) - \sqrt{\lambda - \alpha^0)^2 + 4\alpha^0 (N + \lambda)}}{2(N + \lambda)}\)

we get the following:

\[
\frac{1}{1+\alpha} = \frac{2(N + \lambda)}{2(N + \lambda) - (\lambda - \alpha^0) + \sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0 (N + \lambda)}} =
\]

\[
= \frac{2(N + \lambda)}{(2N + \lambda + \alpha^0) + \sqrt{(\lambda + \alpha^0)^2 + 4\alpha^0 (N + \lambda)}} =
\]

\[
= \frac{2(N + \lambda)(2N + \lambda + \alpha^0) - \sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0 (N + \lambda)}}{(2N + \lambda + \alpha^0)^2 - (\lambda + \alpha^0)^2 - 4\alpha^0 N} =
\]

\[
= \frac{2(N + \lambda)(2N + \lambda + \alpha^0) - \sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0 (N + \lambda)}}{4N^2 + (\lambda + \alpha^0)^2 + 4N(\lambda + \alpha^0) - (\lambda + \alpha^0)^2 - 4\alpha^0 N} =
\]

\[
= \frac{2(N + \lambda)(2N + \lambda + \alpha^0) - \sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0 (N + \lambda)}}{4N^2 + 4N\lambda}.
\]
\[2(N + \lambda)(2N + \lambda + \alpha^0) - \sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0(N + \lambda)} \]

\[
\frac{2N - 2N - \lambda - \alpha^0 + \sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0(N + \lambda)}}{2N} = \frac{\lambda + \alpha^0}{\sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0(N + \lambda)} - (\lambda + \alpha^0)}
\]

\[
\frac{2N\alpha^0}{\sqrt{(\lambda - \alpha^0)^2 + 4\alpha^0(N + \lambda)} + (\lambda + \alpha^0)} = \frac{2N}{1 + \frac{\lambda}{\alpha^0} + \sqrt{(1 + \frac{\lambda}{\alpha^0})^2 + 4\frac{N}{\alpha^0}}}
\]
\textbf{APPENDIX III}

\[ \lambda_0 = \frac{1}{(\text{int})^2} \]

\[ z_{\text{bar}} = \frac{c_*}{c_0 \lambda_0} \]

\[ a = \frac{D_*/D_0 + z_{\text{bar}}}{1 + z_{\text{bar}}} \]

where $D_*$ is a diffusion coefficient of salt, $D_0$ is a polyelectrolyte diffusion coefficient; $z_{\text{bar}}$ is a fitting parameter.

Table A3.1 Data for \(NaCl\) (\(\delta=0.01\) cm; $D_*=1.35 \times 10^{-5}\) cm$^2$/s; $D_0=2.0 \times 10^{-6}$ cm$^2$/s).

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>5</th>
<th>4.4</th>
<th>3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_*/c_0$</td>
<td>1.02</td>
<td>1.84</td>
<td>4.25</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.04</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>$z_{\text{bar}}$</td>
<td>25.50</td>
<td>35.62</td>
<td>55.08</td>
</tr>
<tr>
<td>$a$</td>
<td>1.22</td>
<td>1.16</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Table A3.2 Experimental and predicted data for $c_*/c_0=1.02$

<table>
<thead>
<tr>
<th>$v$ ((\mu m/s))</th>
<th>Measured $\Lambda$</th>
<th>Predicted $\Lambda$</th>
</tr>
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<tbody>
<tr>
<td>2.05</td>
<td>4.18</td>
<td>3.94</td>
</tr>
<tr>
<td>3.08</td>
<td>3.82</td>
<td>3.47</td>
</tr>
<tr>
<td>4.10</td>
<td>3.35</td>
<td>3.08</td>
</tr>
<tr>
<td>6.15</td>
<td>2.56</td>
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<td>2.10</td>
</tr>
<tr>
<td>10.20</td>
<td>1.57</td>
<td>1.84</td>
</tr>
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</table>
Table A3.3 Experimental and predicted data for $c_v/c_0 = 1.84$

<table>
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<th>$v$ (µm/s)</th>
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<tr>
<td>2.05</td>
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<td>3.08</td>
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<td>4.10</td>
<td>3.10</td>
<td>2.94</td>
</tr>
<tr>
<td>6.15</td>
<td>2.64</td>
<td>2.42</td>
</tr>
<tr>
<td>8.20</td>
<td>2.27</td>
<td>2.07</td>
</tr>
<tr>
<td>10.20</td>
<td>1.90</td>
<td>1.82</td>
</tr>
<tr>
<td>12.30</td>
<td>1.62</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Table A3.4 Experimental and predicted data for $c_v/c_0 = 4.25$

<table>
<thead>
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<th>$v$ (µm/s)</th>
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<th>Predicted $\Lambda$</th>
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<td>2.05</td>
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<td>3.08</td>
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<td>2.91</td>
</tr>
<tr>
<td>4.1</td>
<td>2.56</td>
<td>2.69</td>
</tr>
<tr>
<td>6.15</td>
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<td>1.62</td>
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<td>20.52</td>
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<td>1.27</td>
</tr>
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<td>22.57</td>
<td>1.02</td>
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</table>
Table A3.5. Data for KCl ($\delta=0.01$ cm; $D_+ = 1.95 \times 10^{-5}$ cm$^2$/s; $D_0 = 2.0 \times 10^{-6}$ cm$^2$/s).

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>6.5</th>
<th>4.6</th>
<th>3.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1/c_0$</td>
<td>0.83</td>
<td>1.56</td>
<td>3.71</td>
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<tr>
<td>$\lambda_0$</td>
<td>0.023</td>
<td>0.047</td>
<td>0.069</td>
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<td>$Z_{\text{bar}}$</td>
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</tr>
<tr>
<td>$a$</td>
<td>1.24</td>
<td>1.26</td>
<td>1.16</td>
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Table A3.6 Experimental and predicted data for $c_1/c_0=0.83$

<table>
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<td>4.03</td>
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</tbody>
</table>

Table A3.7 Experimental and predicted data for $c_1/c_0=1.56$

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<td>3.89</td>
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<td>3.44</td>
</tr>
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<td>6.15</td>
<td>3.19</td>
<td>2.96</td>
</tr>
<tr>
<td>8.2</td>
<td>2.89</td>
<td>2.57</td>
</tr>
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<td>10.2</td>
<td>2.61</td>
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</tr>
<tr>
<td>12.3</td>
<td>2.29</td>
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</table>
Table A3.8 Experimental and predicted data for $c_\nu/c_0 = 3.71$

<table>
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<th>$v$ ($\mu$m/s)</th>
<th>Measured $\Lambda$</th>
<th>Predicted $\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
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<td>3.00</td>
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<td>2.20</td>
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<tr>
<td>12.3</td>
<td>1.97</td>
<td>1.99</td>
</tr>
<tr>
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<td>1.70</td>
</tr>
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Table A3.9. Data for RbCl ($\delta = 0.01$ cm; $D_z = 2.10 \times 10^{-5}$ cm$^2$/s; $D_0 = 2.0 \times 10^{-6}$ cm$^2$/s).

<table>
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<th>3.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_\nu/c_0$</td>
<td>1.4</td>
<td>2.61</td>
<td>5.38</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.04</td>
<td>0.049</td>
<td>0.077</td>
</tr>
<tr>
<td>$z_{bar}$</td>
<td>35.00</td>
<td>52.85</td>
<td>69.72</td>
</tr>
<tr>
<td>$a$</td>
<td>1.26</td>
<td>1.18</td>
<td>1.13</td>
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</table>

Table A3.10 Experimental and predicted data for $c_\nu/c_0 = 1.4$

<table>
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<th>Measured $\Lambda$</th>
<th>Predicted $\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
<td>4.39</td>
<td>4.32</td>
</tr>
<tr>
<td>3.08</td>
<td>4.22</td>
<td>3.98</td>
</tr>
<tr>
<td>4.1</td>
<td>3.90</td>
<td>3.67</td>
</tr>
<tr>
<td>6.15</td>
<td>3.25</td>
<td>3.13</td>
</tr>
<tr>
<td>8.2</td>
<td>2.75</td>
<td>2.71</td>
</tr>
<tr>
<td>10.2</td>
<td>2.46</td>
<td>2.40</td>
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</table>
Table A3.11 Experimental and predicted data for $c_0/c_0 = 2.61$

<table>
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<th>$v$ (µm/s)</th>
<th>Measured $\Lambda$</th>
<th>Predicted $\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.97</td>
</tr>
<tr>
<td>3.08</td>
<td>3.90</td>
<td>3.71</td>
</tr>
<tr>
<td>4.1</td>
<td>3.67</td>
<td>3.46</td>
</tr>
<tr>
<td>6.15</td>
<td>3.19</td>
<td>3.00</td>
</tr>
<tr>
<td>8.2</td>
<td>2.89</td>
<td>2.64</td>
</tr>
<tr>
<td>10.2</td>
<td>2.61</td>
<td>2.35</td>
</tr>
<tr>
<td>12.3</td>
<td>2.29</td>
<td>2.11</td>
</tr>
<tr>
<td>16.41</td>
<td>1.90</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Table A3.12 Experimental and predicted data for $c_0/c_0 = 5.38$

<table>
<thead>
<tr>
<th>$v$ (µm/s)</th>
<th>Measured $\Lambda$</th>
<th>Predicted $\Lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.05</td>
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<td>2.04</td>
</tr>
<tr>
<td>16.41</td>
<td>1.75</td>
<td>1.76</td>
</tr>
<tr>
<td>20.52</td>
<td>1.51</td>
<td>1.56</td>
</tr>
</tbody>
</table>
APPENDIX IV

Table A4.1 Data for $KCl$ ($D_+=1.95 \times 10^{-5}$ cm$^2$/s; $D_0 = 7.0 \times 10^{-9}$ cm$^2$/s), UFM-100

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>2.5</th>
<th>2.0</th>
<th>1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_0$ (mol/l)</td>
<td>$2.92 \times 10^{-6}$</td>
<td>$2.19 \times 10^{-6}$</td>
<td>$1.46 \times 10^{-6}$</td>
</tr>
<tr>
<td>$c_+$ (mol/l)</td>
<td>$8.00 \times 10^{-5}$</td>
<td>$7.44 \times 10^{-5}$</td>
<td>$8.25 \times 10^{-5}$</td>
</tr>
<tr>
<td>$c_+/c_0$</td>
<td>27.4</td>
<td>33.97</td>
<td>57.19</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.16</td>
<td>0.25</td>
<td>0.31</td>
</tr>
<tr>
<td>$Z_{bar}$</td>
<td>171.25</td>
<td>135.88</td>
<td>185.29</td>
</tr>
<tr>
<td>$a$</td>
<td>17.25</td>
<td>21.45</td>
<td>16.02</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.074</td>
<td>0.09</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table A4.2 Data for $KCl$ ($D_+=1.95 \times 10^{-5}$ cm$^2$/s; $D_0 = 7.0 \times 10^{-9}$ cm$^2$/s), UFM-100

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>3.5</th>
<th>1.3</th>
<th>2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_0$ (mol/l)</td>
<td>$3.65 \times 10^{-6}$</td>
<td>$7.30 \times 10^{-6}$</td>
<td>$5.84 \times 10^{-8}$</td>
</tr>
<tr>
<td>$c_+$ (mol/l)</td>
<td>$7.87 \times 10^{-5}$</td>
<td>$1.00 \times 10^{-4}$</td>
<td>$9.79 \times 10^{-5}$</td>
</tr>
<tr>
<td>$c_+/c_0$</td>
<td>21.56</td>
<td>13.7</td>
<td>16.76</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.082</td>
<td>0.592</td>
<td>0.137</td>
</tr>
<tr>
<td>$Z_{bar}$</td>
<td>264.11</td>
<td>23.15</td>
<td>122.18</td>
</tr>
<tr>
<td>$a$</td>
<td>11.56</td>
<td>116.89</td>
<td>23.72</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.048</td>
<td>0.15</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table A4.3 Data for $KCl$ ($D_+=1.95 \times 10^{-5}$ cm$^2$/s; $D_0 = 7.0 \times 10^{-9}$ cm$^2$/s), UFM-200

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>1.27</th>
<th>1.45</th>
<th>1.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_0$ (mol/l)</td>
<td>$3.64 \times 10^{-6}$</td>
<td>$5.84 \times 10^{-6}$</td>
<td>$9.93 \times 10^{-6}$</td>
</tr>
<tr>
<td>$c_+$ (mol/l)</td>
<td>$5.09 \times 10^{-5}$</td>
<td>$4.05 \times 10^{-5}$</td>
<td>$2.79 \times 10^{-5}$</td>
</tr>
<tr>
<td>$c_+/c_0$</td>
<td>13.97</td>
<td>6.93</td>
<td>2.8</td>
</tr>
<tr>
<td>$\lambda_0$</td>
<td>0.62</td>
<td>0.48</td>
<td>0.51</td>
</tr>
<tr>
<td>$Z_{bar}$</td>
<td>22.53</td>
<td>14.57</td>
<td>5.49</td>
</tr>
<tr>
<td>$a$</td>
<td>120</td>
<td>181</td>
<td>432</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.085</td>
<td>0.057</td>
<td>0.067</td>
</tr>
</tbody>
</table>
Table A4.4 Data for KCl ($D_v = 1.95 \times 10^{-5}$ cm$^2$/s; $D_o = 7.0 \times 10^{-9}$ cm$^2$/s), UFM-200.

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>2.3</th>
<th>1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>c0 (mol/l)</td>
<td>3.64x10-6</td>
<td>7.30x10-6</td>
</tr>
<tr>
<td>c+ (mol/l)</td>
<td>9.22x10-6</td>
<td>8.70x10-6</td>
</tr>
<tr>
<td>c+/c0</td>
<td>2.53</td>
<td>1.19</td>
</tr>
<tr>
<td>λ₀</td>
<td>0.189</td>
<td>0.31</td>
</tr>
<tr>
<td>z bar</td>
<td>13.38</td>
<td>3.86</td>
</tr>
<tr>
<td>a</td>
<td>195.59</td>
<td>577.45</td>
</tr>
<tr>
<td>δ</td>
<td>0.013</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Table A4.5 Data for $K_2SO_4$ ($D_v = 1.95 \times 10^{-5}$ cm$^2$/s; $D_o = 7.0 \times 10^{-9}$ cm$^2$/s), UFM-100.

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>1.75</th>
<th>1.67</th>
</tr>
</thead>
<tbody>
<tr>
<td>c0 (mol/l)</td>
<td>3.65x10-6</td>
<td>5.84x10-6</td>
</tr>
<tr>
<td>c+ (mol/l)</td>
<td>1.23x10-4</td>
<td>9.60x10-5</td>
</tr>
<tr>
<td>c+/c0</td>
<td>33.70</td>
<td>16.44</td>
</tr>
<tr>
<td>λ₀</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td>z bar</td>
<td>103.21</td>
<td>45.85</td>
</tr>
<tr>
<td>a</td>
<td>27.86</td>
<td>60.74</td>
</tr>
<tr>
<td>δ</td>
<td>0.10</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table A4.6 Data for $K_2SO_4$ ($D_v = 1.95 \times 10^{-5}$ cm$^2$/s; $D_o = 7.0 \times 10^{-9}$ cm$^2$/s), UFM-100.

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>1.50</th>
<th>1.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>c0 (mol/l)</td>
<td>3.65x10-6</td>
<td>5.84x10-6</td>
</tr>
<tr>
<td>c+ (mol/l)</td>
<td>3.09x10-5</td>
<td>2.94x10-5</td>
</tr>
<tr>
<td>c+/c0</td>
<td>8.47</td>
<td>5.03</td>
</tr>
<tr>
<td>λ₀</td>
<td>0.44</td>
<td>0.64</td>
</tr>
<tr>
<td>z bar</td>
<td>19.06</td>
<td>7.86</td>
</tr>
<tr>
<td>a</td>
<td>140.55</td>
<td>316.94</td>
</tr>
<tr>
<td>δ</td>
<td>0.05</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Table A4.7 Data for KCl, KNO₃ and K₂SO₄ (\(D_\text{s} = 1.95 \times 10^{-5}\) cm²/s; \(D_\text{b} = 7.0 \times 10^{-9}\) cm²/s), UFM-100.

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>2.5</th>
<th>3.0</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_0) (mol/l)</td>
<td>3.65x10⁻⁶</td>
<td>3.65x10⁻⁶</td>
<td>3.65x10⁻⁶</td>
</tr>
<tr>
<td>(c_+) (mol/l)</td>
<td>4.08x10⁻⁵</td>
<td>6.21x10⁻⁵</td>
<td>6.16x10⁻⁵</td>
</tr>
<tr>
<td>(c_+/c_0)</td>
<td>11.17</td>
<td>17.02</td>
<td>16.88</td>
</tr>
<tr>
<td>(\lambda_0)</td>
<td>0.16</td>
<td>0.11</td>
<td>0.44</td>
</tr>
<tr>
<td>(z) bar</td>
<td>69.81</td>
<td>153.18</td>
<td>37.98</td>
</tr>
<tr>
<td>a</td>
<td>139.38</td>
<td>64.56</td>
<td>252.38</td>
</tr>
<tr>
<td>(\delta)</td>
<td>0.01</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table A4.8 Data for K₂SO₄ (\(D_\text{s} = 1.95 \times 10^{-5}\) cm²/s; \(D_\text{b} = 7.0 \times 10^{-9}\) cm²/s), UFM-200.

<table>
<thead>
<tr>
<th>Intercept (int)</th>
<th>1.20</th>
<th>1.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_0) (mol/l)</td>
<td>3.65x10⁻⁶</td>
<td>7.30x10⁻⁶</td>
</tr>
<tr>
<td>(c_+) (mol/l)</td>
<td>9.29x10⁻⁵</td>
<td>2.71x10⁻⁴</td>
</tr>
<tr>
<td>(c_+/c_0)</td>
<td>25.45</td>
<td>37.12</td>
</tr>
<tr>
<td>(\lambda_0)</td>
<td>0.69</td>
<td>0.51</td>
</tr>
<tr>
<td>(z) bar</td>
<td>36.65</td>
<td>72.76</td>
</tr>
<tr>
<td>a</td>
<td>75.35</td>
<td>38.95</td>
</tr>
<tr>
<td>(\delta)</td>
<td>0.08</td>
<td>0.07</td>
</tr>
</tbody>
</table>
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