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Desalination on Microscale

The Effect of Salt Concentration on the Desalination Performance of a Microfluidic Device

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Abstract

In order to increase the fresh water supply on earth, electrodialysis (ED) is widely used as desalination technology for generating potable water from brackish water. To give a better understanding of this principle, experiments at microscale have been performed in a previous proof-of-concept study at the University of Twente. The used microfluidic device, with hydrogels that mimic the membrane stacks of an ED device, has shown promising results at low concentrated NaCl-solutions.

In this research, the scope is to investigate the compatibility of the hydrogels in the microchip at elevated NaCl-concentrations. A closer look is taken to the influence of higher salt concentrations on the performance parameters: current efficiency and salt removal efficiency. Ion concentration polarisation and the formation of boundary layers play an important role in this investigation. During the experiments, potentiostatic measurements are performed. Several difficulties in the used methods and measurements have led to unreliable outcomes in determining the efficiency of the system. In order to test the proposed hypotheses, an existing numerical model is used to validate the theory. For further research, an optimisation in design of the microfluidic device is recommended.

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1 | Introduction

1.1 Motivation

The scarcity of water gives a major challenge for securing enough fresh water for human, environmental, social and economic demands. To generate potable water, a possibility is to remove salts from seawater or brackish water, also called desalination. This technique is of vital importance in order to increase fresh water supply. A widely used approach for desalination is electrodialysis (ED). To better understand the effects of solutions with different salt concentrations on the desalination performance of larger-scale ED, a microfluidic device with hydrogels as functioning membranes can be used. In a previous research at the University of Twente, a proof-of-concept desalination on a microfluidic device has been tested with low salt concentrations, giving promising results in order to better understand desalination on larger scale [1]. In this research, these devices are tested at higher salt concentrations to investigate the compatibility of hydrogels at these elevated concentrations.

1.2 Scope

The scope of this bachelor assignment is to characterise the effect of different inlet salt concentrations on the desalination performance of a microfluidic device. A closer look will be taken to the following measurable performance parameters: the salt removal efficiency and the current efficiency. In the earlier mentioned proof-of-concept study, the physics of desalination on a microfluidic device has already been performed with low concentration, below 1 mM [1]. In the experiments of this work the same set-up will be used, but experiments with higher concentrated salt solutions (1mM to 10 mM) will be performed. With higher salt concentrated solutions, the amount of salts will be closer to the amount of salts in less ideal brine solutions. In other words the concentrated solutions would be relatively closer to the salt concentrated salt solutions, this will contribute in fundamental research of desalination of brackish water, where hydrogel stacks mimic the ion exchange membranes of an ED stack.

1.3 Report structure

This report starts with an explanation of theoretical principles that play an important role in desalination processes, followed by the experimental plan. After that, the results in combination with discussion is presented. Finally, an overall conclusion and recommendations are given.

2 Theoretical framework

The background theory of ion-exchange through a membrane system will be explained. First, an introduction will be presented of the main principle: electrodialysis. Followed by information about ion concentration polarisation, current density and the different current regimes.

2.1 Electrodialysis

Electrodialysis (ED) can be used as a technique for the desalination of brackish water sources. A schematic overview of this ED process is given in Figure 2.1. It is a separation process technology, where a feed stream flows through (spacer) channels which separate a series of alternating cation and anion exchange membranes. These membranes are of opposite charge in comparison with the ions that will pass them. The exclusion of co-ions, ions with the same charge as the membrane, is called the Donnan exclusion. The electroneutrality in the membrane and the solution is disturbed, because of the fact that ions carry a charge [2]. In addition, an electric field is applied over the membrane stacks. Ions are moving in the electric field towards the electrode with opposite charge, but are selectively blocked by the membranes. When this process of ion exchange has taken place over a certain amount of membrane area, the outflows will be split into depleted and enriched salt streams [3]. An advantage of ED is that it is easy to scale and therefore it is very useful for small-scale desalination experiments. In this way, fundamentals of ion transport phenomena near membranes can be investigated at microscale.



Figure 2.1: Principle of electrodialysis where the driving force is the electrical potential [4]. CEM and AEM stands for cation and anion exchange membranes, respectively.

In the ideal case, the cation exchange membranes will only conduct the cations while the anion exchange membranes will only conduct the anions, due to ion selectivity. If a membrane is fully permselective, the counter-ions will carry all the current in the membrane. The transport number of this counter-ion equals one [2]. The transport number (t_i) is defined as the current that is carried by the ion divided by the total current. Nevertheless, membranes do not have this behaviour of full permselectivity, so co-ions and water also pass them, which leads to reduction of performance.

2.2 Ion Concentration Polarisation

For the ion transport in ED-systems, three ion fluxes are involved: the convective flux as a result of convection perpendicular to the membrane, a diffusive flux resulting from a concentration gradient and a migrative flux in the electric field [2, 4]. These three parts are visible in Equation (2.2.1).

$$J_i = vC_i + D_i \frac{dC_i}{dx} - \frac{z_i F C_i D_i}{RT} \frac{d\phi}{dx}$$
(2.2.1)

In this equation J_i represents the flux of a specific ion *i*, and v and C_i represent the convective transport velocity and concentration, respectively. D_i is the diffusion coefficient of the specific component, which is multiplied by the derivative of the concentration in the horizontal x-direction in order to gain the diffusive flux. z_i indicates the valence of the component, F and R represent the Faraday and gas constant, respectively, followed by the Temperature (T). To get the migrative flux, this whole term is multiplied by the derivative of the electrical potential over the x-direction. In comparison with the other fluxes, the convective flux can be neglected, because the membranes are non-porous and there is thus no convective flow through the membranes. In this way, Equation (2.2.1) becomes similar as the Nernst-Planck equation, where ion transport over ion exchange membranes are only depending on two driving forces: the concentration and the electrical potential.

Ion Concentration Polarisation (ICP) is a phenomenon that limits the ion-exchange process through the membranes, which negatively influences the performance of an ED system because of the increasing electrical resistance of the solution [5]. It is desirable to work at the highest current density, to have a maximum ion flux over the membranes, but this becomes difficult due to ICP [2]. The reason of this phenomenon is the difference in the earlier mentioned transport numbers of the solution and the membrane. In the solution it can be assumed that t_i for the cations and anions are roughly similar, but in the permselective membrane the current is largely carried by the counter ion. Due to this, a boundary layer is formed at the interfaces of each side of the membrane. Between the desalting membrane surface and the (diluate) solution, the salt concentration will be relatively more depleted in the boundary layer. On the other side where the solution is enriched with ions, the concentration in the boundary layer will be relatively increased. This concentration profile is presented in a simple outline in Figure 2.2. C^b indicates the solution or bulk concentration and C^m indicates the concentration at the membrane surface. Only the ion fluxes on the left side are presented. Where J_{+}^{dif} and J_{+}^{mig} represents respectively the driving force of diffusion and migration of the positive counter-ion, which is visa verse also valid for the negative co-ins. Furthermore, electroneutrality over the whole system is assumed.



Figure 2.2: Schematic representation of ion concentration polarisation over a cation exchange membrane, with the conduct of the concentration profile in the boundary layer [2].

This ICP phenomenon will lead to a voltage drop, also called 'internal resistance', across the electrolyte [6]. The appearance of this transition is generally observable in current-voltage curves (IV-curves). At a certain potential the limiting current is reached, due to ion concentration polarisation. This limiting current will further be explained in Section 2.3. To reduce ion concentration polarisation, the flow rate could be increased in order to promote turbulence around the membranes, which will result in better mixing and a reduced thickness of the boundary layer.

2.3 Current density

In the membrane, the driving diffusional force can be neglected [2]. This is because the charge concentration in the membrane is relatively large in comparison with that of the solution. As a result, only the migrative part of Equation (2.2.1) is assumed to be valid in the membrane. With this assumption, the ratio between the positive and the negative ion flux (J_+ and J_-) is equal to the ratio of the ion transport numbers (\bar{t}_+ and \bar{t}_-) in the membrane:

$$\frac{J_+}{J_-} = \frac{-\bar{t}}{1-\bar{t}_+} \tag{2.3.1}$$

For this equation, it is assumed that the electrolyte solution only contains univalent ions ($C_+ = C_- = C$). The sign in Equation (2.3.1) is negative, because the fluxes are vectors and have an opposite direction from each other, while the transport numbers are always taken positive.

In the boundary layer the diffusion flux does play an important role. So, the flux for both ions which has already been described in Equation (2.2.1) (without the convective part) is valid. To determine the current density, a steady state situation is considered. In this case, the fluxes in the membrane equal the fluxes in the boundary layer. Where the ionic diffusion coefficients from Equation (2.2.1) can be rewritten to the diffusion coefficient of the electrolyte D, see Equation (2.3.2). In the solution the ratio of the ionic diffusion coefficients (D_+ and D_-) is equal to the ratio of the solution transport numbers (t_+ and t_-).

$$D = \frac{2D_+D_-}{D_+ + D_-} = 2D_+(1 - t_+)$$
(2.3.2)

When all above mentioned equations are combined, the current density (*i*) can be determined with the help of Faraday's law, where *i* equals the Faraday constant times the difference in ionic fluxes. The rewritten equation, which is also integrated over the boundary layer thickness (δ), is as follows:

$$i = \frac{FD}{\bar{t}_{+} - t_{+}} \frac{C^{b} - C^{m}}{\delta}$$
(2.3.3)

In Equation (2.3.3) F represents the Faraday constant, D is the diffusion coefficient, \bar{t}_+ and t_+ are respectively the positive charged transport numbers of the membrane and the solution and C^m and C^b are respectively the concentrations at the membrane surface and in the solution. In this equation, the following assumptions are made: the transport numbers and the diffusion coefficient are constant over x. In this way, the concentration gradient in the boundary is also constant. When *i* is increased, the difference between C^m and C^b becomes larger, because C^m decreases. At a certain *i*, C^m will reach zero. At this point, the limiting current density (i_{lim}) is reached. This transition in current behaviour will be explained in the following sections.

2.4 Current regimes

The behaviour of the current in IV curves can be distinguished into three current regimes, see Figure 2.3. These regimes will shortly be explained.



Figure 2.3: Conceptual representation of the relation between the current through a membrane and the corresponding voltage drop over the membrane and their boundary layers [7].

Ohmic regime

In the first regime, the Ohmic regime, the current density is low. There is a positive linear relation between the current and the voltage drop over the membrane [7, 8]. In this case Ohm's law is valid, which allows that the effective resistance of the membrane system can be deduced from the slope of the IV-curve. As mentioned in Section 2.3, there is no depletion or ion enriched layer formed on each side of the interface of the hydrogel yet. This is also visible in Figure 2.3. The curve has the largest slope in the Ohmic regime. With Ohm's law is derived that the resistance is low in this regime, as follows that the conductivity over the system is high. Hence, in this regime the current efficiency is most ideal.

Limiting regime

In this regime the limiting current density is reached, which has already been explained previously. The limiting regime is attained when the current does not increase with the electric field strength due to ion concentration polarisation. As a result, the process efficiency will be limited [2]. This regime is shown in Figure 2.3 as a flattened plateau.

Over-limiting regime

In this regime, corresponding to the right side of Figure 2.3, the overlimiting regime is entered. Theoretically, no higher currents can be expected after the limiting current. However, in practice this does not yield [2] due to the following phenomena: water-splitting and electroconvection [1, 7, 9]. Water-splitting and other hydrodynamic effects take place at the interface between the depletion zone and the membrane. With electroconvection (electro-driven vortices) the depletion zones are mixed with the conductive bulk of the electrolyte. These phenomena will not further be explained, because it is out of the scope of this assignment. The main focus for this assignment is to determine the efficiency in the Ohmic regime, because in the overlimiting regime efficiency loss for the ED system is developed due the mentioned phenomena.

3 | Experimental plan

This part of the report is split in experimental theory and an overview of the methods and measurements.

3.1 Experimental Theory

Microfluidic device

In the experiments, charged hydrogels will be used as anion and cation membrane interfaces, which simulate the membranes in ED stacks [1]. In Figure 3.1 a schematic representation of this micro chip is given.

A problem that could be faced using membrane stacks at micro scale, is the challenging fabrication, because of robustness and difficulties in consistency [1]. This could for example lead to liquid leakage. Because of these reasons, hydrogels give a good alternative for the membrane stacks. It can be incorporated relatively easy in the microfluidic device and it makes the device less expensive. Furthermore, hydrogels provide good study towards the hydrodynamic and ion transport phenomena in microfluidic devices. To place the hydrogels in the device, a capillary line pinning technique is used for controllable patterning.



Figure 3.1: Schematic representation of microfluidic device [1].

For the experiments, the original type of the microchip is used. It contains six microchannels, each with a separate inflow. The dimensions are given in Table 3.1.

Original shape	Length/width of	Dimensions (in μ m)
	Channel in y-direction Channel at hydrogel in y-direction Hydrogel in y-direction Hydrogel in x-direction PDMS pillar in x-direction	690 867 1550 690 690

Table 3.1: Schematic representation of micro chip with dimensions.

The microchip consists of hydrogel pillars and capillary barriers [1]. The components of the hydrogel pillars are made of polydimethylsiloxane (PDMS) and are interlinked by six microchannels. To create a charge selective interface in the AEHs and CEHs, the charged monomers [2-(methacryloxyloxy)ethyl]trimethylammonium chloride (METC) and 3-sulfopropyl acrylate potassium salt (SPAP) are used. In order to form METC and SPAP polymers, the monomers are photo-polymerised with acrylamide, N,N'-bis(2-hydroxyethyl)-ethylenediamine (bis) and free radicals yielded by 2,2-dimethoxy-2-phenylaceto-phenone (DMPA). Advantages of these polymers are that they have a high swelling degree, the hydrogels can absorb a high water content, and they have a good hydrolytic stability, which provides charge-based separations in micro chips. Moreover, the polymers have permanent positive and negative charge densities, which are independent in a large pH range (pH of 2-12). However, the permselectivity of the AEHs and CEHs have a moderate percentage of respectively 29 and 26%, due to the capability of absorbing large amounts of water. The moderate permselectivity of the hydrogels will negatively influence the desalination and current efficiency. How to determine these efficiency values, will later on be discussed in this section.

Salt solutions

To handle fresh water supply by electrodialysis, as mentioned in the 'Introduction', a microfluidic device is used to better understand the concept on smaller scale. In order to use the microfluidic device in the experiments, salt solutions are used to better mimic the concentrations of brackish water. The classification of water with associated dissolved salts are given in Table 3.2. In the experiments, lower concentrations will be researched (0.1 to 5.0 mM, equal to 6 to 292 ppm) to determine if the device works in this concentration range. Brackish water consists of different types of salts. However, due to the short period of time for this bachelor assignment, no differentiation will be used in the solutions. The experiments will be limited to different concentrated NaCl-solutions.

To visualise the ion transport through the hydrogels, a negatively charged fluorescent dye, Alexa Fluor 488 Cadaverine, is used [1]. In the measurements of the 0.1 mM NaCl solution, 5 μ M fluorescent dye is used. This way, when using the microscope, the positively charged AEHs will respectively light up more intensively, due to the fact that the negatively charged dye behaves as counter-ion through these hydrogels.

Designation	Total dissolved salts (ppm)
Fresh water	<500
Slightly brackish	500 - 1000
Brackish	1000 - 2000
Moderately saline	2000 - 5000
Saline	5000 - 10000
Highly saline	10000 - 35000
Brine	>35000

Table 3.2: Classification of water based on concentration of salts [10].

Efficiency determination

After performing the experiments, the parameters current efficiency and salt removal efficiency can be determined to see whether or not the desalination performance will deteriorate.

With the current efficiency (CE) the optimum range of applicability of an ED cell can be determined [11]. Besides this, the total area that is required for the desalination can be subtracted from this efficiency. CE describes how well ions are transported over the membranes when a certain current is applied. In Equation (3.1.1) the determination of CE is given over one cell pair, in which the difference between the inflowing ions in the channel per second and the outflowing ions in the desalinated channel per second is divided by the total ion transport per second.

$$CE(\%) = \frac{zF\Phi_f(C_{in} - C_{out,des})}{N_i N_c I_{avg}} \cdot 100$$
(3.1.1)

In the above equation the value of z equals 1, because monovalent ion solutions are used during the experiments. F is the Faraday constant (96485 C/mol) and Φ_f is the flow rate in m³/s. C_{in} and $C_{out,des}$ represents respectively the concentration of the inflow and of the desalinated outflow (in mol/m³). The channels which have a desalinated outflow are channel 3 and 5 of Figure 3.1a. Furthermore, N_i equals the number of available ions in the solution, which equals 2 (Na⁺ and Cl⁻) and N_c is the number of cell pairs, which equals 1 in this study. I_{avg} is the average current (in A), which is determined in the experiments by performing a chronoamperometry measurement.

In order to calculate the other desalination performance parameter, the salt removal efficiency (RE), Equation (3.1.2) can be used (BRONBOEK). Also in this equation, C_{in} indicates the concentration of the inflow (in mol/m³) and C_{out} indicates the concentration of the outflow (in mol/m³).

$$RE(\%) = \frac{C_{in} - C_{out,des}}{C_{in}} \cdot 100$$
(3.1.2)

With the experiments, the outcomes of $C_{out,des}$ and I_{avg} will change due to the variation of different variables. This will have an impact on the desalination performance parameters.

3.2 Methods & Measurements

Set-up & Variables

In Figure 3.2 the experimental set-up is shown. In the experiments, three microfluidic pumps with six syringes are required to pump different salt concentrated solutions through the six micro channels. The pumps are connected with six polymeric tubing to the micro chip. The end of the chip is also connected with plastic tubing, where the outflow is collected on a petri dish. The outflows are captured in separate plastic vials in order to determine the outflow concentration of each channel. To visualise the ion exchange through the hydrogels, an optical microscope is used with fluorescent dye. Furthermore, channel 1 and 6 are in the middle connected with two electrodes to the NOVA Metrohm Autolab instrument. With this instrument, different potentiostatic measurements can be performed in order to test the desalination performance with different concentrated salt solutions.

An important variable that will be changed during the experiments is the concentration of the inflow. The experiments will be performed with different concentrated sodium chloride solutions: 0.1, 1, 2, 5 and 10 mM. Another important variable that can be varied is the flow rate. For the measurements two different flow rates will be examined, namely: $3 \mu L/min$ and $6 \mu L/min$. The voltage can also be varied between 0 and 10 V.



Figure 3.2: Set-up for the experiments.

Measurement procedure

At first, the hydrogels of the chip have to be fully saturated with the prepared concentrated salt solution to reach a steady state situation in order to perform NOVA measurements. The flow rate of the pumps are set at a constant value of 3 or 6 μ L/min. After reaching steady state, an IV diagram can be made over the whole microchip. In this way, the characteristic Ohmic, limiting and overlimiting current regimes will be determined. This measurement can be done by using the *LSV staircase* measurement tool from NOVA. With this tool, a linear sweep voltammogram is performed with a staircase profile in a potential range of 0 to 9 V [12]. The IV sweeps will be performed in triplicate. In order to determine the ion concentration of the collected salt enriched or depleted outflows from channel 2 to 5, a chronoamperometry measurement can be used. The outflows of channel 1 and 6 will not be collected, because of the ion reactions near the electrodes which would give a distorted image. During the chronoamperometry measurement a constant potential is applied. Because the scope of this bachelor assignment is to look at low voltages in the Ohmic regime, a potential of circa 0.5 V is used. Meanwhile, the current signals are recorded over a period of approximately 1400 seconds. When the measured data points have reached a flattened curve profile in the time versus current diagram, the outflows of each channel is captured in plastic vials.

Processing experimental data

In order to determine the outflow ion concentration of the channels, two different methods can be used: IV sweeps or FRA impedance measurements in combination with a fitting model. These methods will shortly be introduced in this section.

When the method of IV sweeps is used, the same order of proceedings are applicable as described in Section 3.2. In the Ohmic regime, the slope of the IV curve is equal to the resistivity, which is the reciprocal of the conductivity. When a linear calibration curve is made with known concentrations versus the conductivity, the ion concentrations of the outflow of each channel can be determined. This method is a less accurate way to determine the ion concentration, because the resistance has to be determined in the Ohmic regime. This leads to inaccuracies when verifying the slope, due to difficult observation of transition of the current regimes.

The other method that can be applied in order to determine the ion concentrations is with the use of the *FRA measurement* tool in NOVA, that can be used to perform impedance spectroscopy measurements through a frequency scan. After collecting these data, the Fit & Simulation tool in NOVA is used to determine the resistivity. An example of a fitted curve, the Nyquist plot, can be found in Figure 3.3. In this Figure $-Z_{real}$ and $-Z_{imaginary}$ represent the observed real and imaginary impedances. In Figure 3.3b the used equivalent-circuit model of the electrode is given, also called the Randless circuit [13, 14]. In this Figure, R_s represents the resistance of the solution, R_{ct} is the charge transfer resistance, C_{dl} is the double layer charging at the electrode surface and W is the Warburg Element. The Warburg Element shows the diffusion of ions in a solution. So, it contributes at low frequencies ($\omega \rightarrow 0$) in the diffusionally controlled region (right side of Figure 3.3a). If ϕ equals 45°, infinite Warburg diffusion is arising. The required charge transfer resistance equals the diameter of the fitted semi-circle equals. This value (R_{ct}) can be determined by subtracting R_s from the resistance of both the solution and the resistance due to charge transfer ($R_s + R_{ct}$). These points intersect the Z_{real} axis where $-Z_{imaginary}$ equals zero, see Figure 3.3a.

After performing these measurements, the conductivity can be verified by taking the reciprocal of the resistivity. To determine the ion concentrations of the outflow of each channel, a calibration curve has to be made. In this plot, known concentrations are plotted with their corresponding determined conductivity. This will result in a linear calibration curve.





Accuracy analysis

To show how accurate the experimental data is, an error analysis will be performed. The plotted average results of the IV sweeps will be presented with a shaded symmetric error bar in Matlab. This error bar is based on the standard deviation of the current. It is possible that the standard deviation is estimated too high, because the experiments are performed in triplicate in stead of more measurements. The same sort of accuracy analysis will be used for the determination of the ion concentration.

Model procedure

To qualitatively compare the experimental results with the theory, a numerical model is used. This model is created by the research group Soft Matter, Fluidics and Interfaces in the Multiphysics software COMSOL 5.2. The model results will be based on a flow rate of 3 μ L/min, 6 μ L/min or no flow, where fully saturation is assumed.

With this model a couple of outputs will be generated. Firstly, a velocity profile through the channel over a specific potential in the Ohmic regime will be made. Secondly, a graphical representation can be made of the concentration profiles over the whole channel in x-direction (see Table 3.1), based on the flow rate (0, 3 and 6 μ L/min). Furthermore, a concentration profile is given over the part of the channel where ion exchange will take place, the part that is enclosed by the hydrogels. Because the concentration changes over time, the time dependency will also be presented in the plot. For clarification is in Figure 3.4 the maximum width of the channel (y-direction) displayed. The position at the bottom of the component equals 0 μ m and at the top the maximum value of the position is 867 μ m. A point that should be made is that in the model, the width is made non-dimensionalised. A closer look will be taken to see if there is a difference in concentration profile if different flow rates are used (3 vs 6 μ L/min) and if different channel components are observed (c3 vs c5).



Figure 3.4: Numbering of channel components and the width size in y-direction.

The model is based on Poisson-Nernst-Planck and Navier-Stokes equations. The boundary conditions are as followed: a constant concentration on the wall of the hydrogel is set and no ion transport takes place on the PDMS patches. The model will not be explained in further detail, because it is out of the scope of this assignment.

3.3 Hypotheses

With the background information that is gathered so far, several hypotheses can be made. The hypotheses will shortly be explained in this section. These hypotheses will be tested during the experiments. The confirmation or rejection of these hypotheses will be discussed in Section 4.

When looking at Equations (3.1.1) and (3.1.2), I suppose that the efficiency parameters will not change with higher inflow ion concentrations (C_{in}). When a chronopotentiometry measurement is performed at higher concentrations of the inflow, more ions are available, so I_{avg} will become higher. I suppose that the current efficiency will remain constant, because the increase of C_{in} will be levelled out with the increased value of I_{avg} . Furthermore, the salt removal efficiency will also be constant over the range of different values of C_{in} . Assuming that the performance of the ion exchange through the hydrogels will not be affected by higher concentrations and work the same as at low inflow concentrations.

Besides determining the desalination performance parameters, I will look at the IV curves at different concentrated NaCl-solutions and flow rates. At higher concentrations of the inflow, the current will be relatively higher at a certain potential. This is due to the simple fact that more ions are available to carry the current through the hydrogels. For this reason, I suppose that the slope of the IV curve is larger in the Ohmic regime when higher concentrated NaCl solutions are used.

With the difference in flow rate, I presume that a similar situation is valid. Because more ions are pumped into the channels when a higher flow rate is used, the current will be relatively higher at a certain potential. This result in a steeper IV-curve in the Ohmic regime.

In the model part, I will look at the concentration profile over the y-direction of the width of a channel component over time. First, I will look if there is a difference when no flow is used or a set flow rate of 3 μ L/min. I presume that the depletion zones will be larger when no flow is applied. When I look if the flow rate influences the concentration profile over time, the same expectation is made. I suppose that at higher flow rates less depletion zones are formed, due to the fact that it promotes turbulence around the hydrogel surface in the channels. In this way better mixing of ions takes places. So, at higher flow rates a relatively small edge with high concentration at the interface of the hydrogel is formed in comparison with lower flow rates. A larger part in the middle of the width of the channel component would have a similar concentration at higher flow rates, because less depletion zones are formed at higher flow rates.

At last, I will look whether the chosen channel component (c3 or c5) has influence on this concentration profile. I expect how further the chosen channel component is away from the fresh feed, the larger the depletion zone would be at the edge of the hydrogel. As explained with higher flow rates, a larger middle part of the width of the hydrogel will have the same concentration with c3 in comparison with c5. I presume that this is because at the beginning of the channel a small depletion zone is developed at the hydrogel interface, which will spread out over the edge towards the second channel component. In the second channel, the depletion zone will grow further on this small layer from c1. This results in a relatively larger depletion layer. This built up of depletion layers will become larger throughout the channel.

4 **Results & Discussion**

In this section, the results of the experiments and model are presented together with the discussion. Besides this, the proposed hypotheses will be confirmed or rejected and an analysis of the used procedure and processing methods will be given.

4.1 Experimental results

Visualisation of formation of depletion zones

In Figure 4.1 the progression of depletion zones in the channels of the microfluidic device can be seen over time. In a period of circa 15 seconds between two frames, dark zones are created around the lower edge of each micro channel. Before the Chronopotentiometry measurement was started, the channels were fully saturated with a 0.1 mM NaCl solution containing fluorescent dye. When no air bubbles were visible in the channels, the flow rate was turned off. The full saturation of the microchannels is presented in the first image. In the consecutive images the growth of the depletion zones are visible, this is due to the applied potential of 8 V.



Figure 4.1: Formation of depletion zones in the channels due to an applied potential of 8 V without a set flow. The time span between two frames is circa 15 seconds.

In experiments with fluorescent dye, only a 0.1mM solution is used and not higher concentrated solutions. The reason is that at higher concentrations depletion zones will still be developed, but in a longer period of time. Why this occurs, will be explained later on.

Electrical characterisation of the system

In the first graph, Figure 4.2, the average IV sweeps with a standard deviation error box can be found for a flow rate of 3 μ L/min. For each concentration of the inflow, IV measurements were performed in triplicate. The average IV sweeps with standard deviation for 6 μ L/min can be found in Figure A.1 of the Additional figures in Appendix A. The IV sweeps at higher concentrations are left out in this graph, because these measurements failed at the flow rate of 6 μ L/min.



Figure 4.2: Average IV sweeps with standard deviation error boxes of different inflow concentrations at a flow rate of 3 μ L/min.

What can be seen from Figure 4.2 is that the current increases at higher ion concentrations, which supports the hypothesis that is made. Since the charged ions facilitates the conductance of the current, the conductivity has a positively linear relation towards ion concentration. So, a larger slope in the Ohmic regime indicates a lower resistance and hence a higher conductivity. In spite of this, it is shown in the figure that in the Ohmic regime the curves lay very close to each other and the distinction is not large. A point that should be noticed is that during the measurements no off-set potential is used. This results in the fact that not all the IV-curves start at point (0,0), due to an error in the used system. At low potentials, the standard deviation error margin is also large at low potentials.

Furthermore, the distinction of the three current regimes is hardly to see in each curve, especially for the 0.1 mM NaCl-solution. Around the 1.7 V a possible transition of the Ohmic to the limiting regime can be seen for the concentrations of 2 and 5 mM. For the concentrations of 5 and 10 mM this transition is around 3 V. The limiting current (i_{lim}) is reached when the concentration at the surface of the membrane (C^m) becomes zero. Because at higher ion concentrations more ions are available, it will take longer before C^m reaches zero. So, when a similar potential is set at higher concentrations, the formation of depletion zones will arise slower. Hence, at a higher potential, i_{lim} will be reached. What also can be seen from Figure 4.2 is that the limiting current regime is not visible as a flattened plateau, which was described in the theoretical part of this report. A possible argumentation could be that in an earlier stage electrode reactions and water splitting take place. Moreover, the transition of the limiting to the over-limiting regime is also hard to see in Figure 4.2. Around an applied potential of 4 V, a small node in all the curves are visible. It can also be seen, that at potentials of 7 to 8 V the curves have more fluctuations. This is due to effects of electrode reactions, water splitting and other hydrodynamic effects that take place in the overlimiting regime. Another visible point with the same explanation, is the larger fluctuations in this regime of the triplicate measurements for all the concentrations.

In Figure 4.3 two Chronoamperometry measurements are visible, one with an inflow concentration of 0.1 mM NaCl and the other with an inflow concentration of 5 mM NaCl. The current is measured when a potential of 2 V was applied, during a period of 700 seconds.



Figure 4.3: Chronoamperometry measurements of two different concentrations of the inflow with an applied potential of 2 V. The connecting lines are for visualisation purposes only.

As can be seen in Figure 4.3, a higher current is reached for the 5 mM NaCl-solution. As explained before, the current increases when the amount of ions increases. Notable is that at higher ion concentrations, more fluctuations are shown in Figure 4.3. During the experiments, it was hard to perform a whole measurement at 5 mM and 10 mM, because often the electrode was pushed out the micro chip before steady state was reached. A reason for this could be the low charge density of the hydrogels. The charge density of the hydrogels are not high, respectively 0.43 ± 0.10 and 0.14 ± 0.02 mol/L_{H₂O}. Considering that the ion-selective hydrogel is related to the charge density of the hydrogel, ion selective transport will decrease at higher concentrations. Whether this is true, could be validated with the outcomes of the desalination efficiency's. The efficiency should be less at higher concentration in comparison with lower concentrations. However, it was not possible to determine the desalination efficiency, due to measurements problems. These problems will be discussed in Section 4.3.

In Figure 4.4 a comparison between the two flow rates (3 & 6 μ L/min) is presented. The used solutions are concentrated with 0.1 mM, 1 mM and 2 mM NaCl.



Figure 4.4: Comparison of average IV sweeps for a flow rate of 3 & 6 μ L/min for three different inflow concentrations.

What can be seen in Figure 4.4 is that the curve is relatively steeper at higher flow rates as to lower flow rates. At higher flow rates, more ions are pumped through the channels per unit of time. Which has as consequence that less depletion zones are formed around the interfaces of the hydrogel components. A higher flow rate ensures an increase of the current at a given potential. This could also be caused by extensive electrode reactions or gas formation [1]. This phenomena could show up at high flow rates and high concentrations. Which could be the case, because the measurements at higher concentrations with 6 μ L/min failed. Despite the fact that the current increases, the salt removal efficiency could decrease. When the flow rate is set too high, ion exchange would not take place in a sufficient way. Unfortunately, this efficiency could not be determined during the experiments.

4.2 Modelling results

In this part, the modelling results are presented and discussed. All results are based on the original shaped chip. This section can be divided in two categories of results based on a set flow rate or no flow.

With flow

In Figure 4.5 two profile gradients over the whole channel are visible. These parameters are made dimensionless. Furthermore, a potential of 2 V is applied and the flow rate is set on 3 μ L/min. The profile gradients were made at steady state, where the time (t) equals 0.01 s. The upper part of the Figure, represents the velocity profile over the x-direction and the lower part shows the concentration gradient.



Figure 4.5: Normalised velocity and concentration profile with an applied potential of 2 V and a flow rate of 3 μ L/min (t = 0.01 s).

In the upper side of Figure 4.5 is shown that the velocity (in x-direction) in the middle of the channel is alternately high (red) and less high (orange). At the place where ion exchange take place, between the channel component and the hydrogel, the channel has a larger width. The ions are spread over a larger area when ion exchange takes place. Hence, the velocity will momentarily decrease, where it will increase again in the space between the channel components. Another visible remark for the velocity profile, is that at the ion exchange interface of the channel and the hydrogel the velocity profile gradient is blue, which indicates a very low to zero velocity. This is due to a set boundary condition, which implies that the wall of the hydrogel stands still. Due to low fluid velocities, a depletion layer is easily formed. In the lower part of Figure 4.5 the concentration profile is shown. The depletion layer at each channel component is becoming larger throughout the channel, which confirmed one of the hypothesis that is made. As can be seen in the figure, the depletion zone of c1 integrates with c2, where a larger depletion zone is visible. This integration of boundary layers increases over the whole channel.

In Figure 4.6 the concentration profile over the width of channel component 5 (c5) over the time is presented. How the position on the width is established, was schematically presented in Figure 3.4. For the plot in Figure 4.6 a flow rate of 3 μ L/min is used. The same plot is made for a flow rate of 6 μ L/min, which is presented in A.2 in Appendix A.



Figure 4.6: Dimensionless concentration profile over y-direction of channel component 5 including time dependency (applied potential is 2 V and the flow rate is 3μ L/min).

In Figure 4.6 the graphical representation of channel component 5 of Figure 4.5 is shown, with time dependency. At the start (t = 0 s), the concentration over the channel component is equally divided. It can be observed, that as function of time the depletion layer at the interface of the hydrogel increases. Hence, the depletion zone, and at the other side of the channel, the ion enriched zone increases. Over time the curve is pressed, which indicates that the middle part (with similar concentration) becomes smaller over time.

Figure 4.7 gives a comparison between location and flow rate versus the concentration profile.



Figure 4.7: Comparison of dimensionless concentration profile over y-direction between flow rates and channel components (applied potential is 2 V and t = 0.01 s).

From Figure 4.7 several observations can be made. At first, it is shown that at a low flow rate (blue and yellow lines) the curve is more pressed, because the boundary layers are thicker at lower flow

rates. This result supports the hypothesis that at higher flow rates the depletion zones will be smaller. Besides that, the ion enriched zones will also be smaller.

When you compare the different channel components with each other at a similar flow rate (blue and yellow or green and red) it is visible that the curves of c5 are more pressed then those of c3. This is due to more depletion formation at the last hydrogel channel, which was also shown in and explained with Figure 4.5.

Another conclusion that can be drawn from Figure 4.7 is that more depletion is formed in c3 with a flow rate of 3 μ L/min (blue line) than at c5 with a flow rate of 6 μ L/min (red line). Which indicates that the location has more influence on the desalination than the flow rate. So, when the hydrogel stacks and channels are made longer, more ion exchange could take place. Hence, a better desalination performance is reached.

No flow

In Figure 4.8 the concentration profile over the width of hc 1 over the time is given when the flow is turned off. By the reason of no flow, it does not matter for which channel component this plot is made. Moreover, a potential of 0.5 V is applied.



Figure 4.8: Dimensionless concentration profile over y-direction of channel component 1 including time dependency (applied potential is 0.5 V without a set flow).

In Figure 4.8 it is clearly shown that in a short period of time large depletion zones are formed. At the last time curve, t = 0.05 s, approximately half of the channel component is depleted. This plot can not accurately be compared with Figure 4.7, because in this case a potential of 0.5 V is applied in stead of 2 V. However, with a higher applied potential the current will increase which will result in the fact that ion exchange will take place faster. Hence, the depletion zones will be formed faster, which would not give an equal spread line figure as in Figure 4.8. Otherwise smaller time steps should be taken.

4.3 Discussion of Methods & Measurements

Unfortunately, it was not possible to determine the desalination performance parameters, which was in the scope of this research. Due to measurement errors in the set-up, the current and salt removal efficiency could not be determined. The calibration curve did not gave a linear relation between the concentration and the conductivity. When using this curve, the measured concentrations of the supposed to be enriched outflows were giving desalinated values, hence 'concentration loss' was arisen. So, the calibration curve could not be used for the experiments due to errors in the two selected methods: FRA impedance measurements and the slope of the IV-curve.

In the case of the FRA impedance measurement, the Fit & Simulation tool gave large errors in the fitted curve in comparison with the measured data points. Thereby, the fitted curve showed a negative resistance of the solution, which cannot be valid. Regarding the second method, the conductivity was determined by the slope of the IV-curve in the Ohmic regime. From Figure 4.2 is visible that these curves are all very close to each other, even the standard deviation error boxes overlap each other. Mainly at high concentrations (5 and 10mM NaCl) the triplicate measurements were fluctuating in the Ohmic regime. Hence, both methods for determining the concentration of the outflows of the channels did not work as expected. As a consequence, the current efficiency and salt removal efficiency could not be determined with the used set-up and methods.

This reasoning can also be confirmed with observations during the measurements. When the experiments were performed, several micro chips were used due to leakages at the in- and outlets and at the locations where the electrodes were inserted. Mainly near the electrode, accumulated concentrated droplets were formed. There was unintended contact with the air due to leakages. This led to air bubbles near the electrode, which also effected the measurements. The leakages were retained by melted candle wax, but at higher concentrations and higher flow rates this did not work. As a result, chronoamperometry measurements could not take place at high concentrations and the IV sweeps gave very fluctuating results. So, at higher concentrations the hydrogels of the microfluidic device were not compatible.

5 Conclusion

The main goal of this research was to investigate whether the hydrogels of the used microfluidic device would manage higher concentrated NaCl-solutions. This had to be researched by determining the current efficiency and the salt removal efficiency, which both are based on the concentrations of the desalinated outflows. Some difficulties occurred during the experiments, including liquid leakages, air bubble formation and difficulties in determining the outflow concentrations. Nevertheless, other measurements are performed in order to test the hypotheses. In order to justify these hypotheses, IV-and chronoamperometry measurements were performed. Besides this, an existing numerical model was used to support the theory.

From the IV-curves and the chronoamperometry plot can be noticed that the current is increased with higher concentrations and higher flow rates. More charged ions (per second) are available to carry the current through the device. Because more ions are pumped into the channels, the formation of depletion zones will take longer. Hence at higher potentials, the transition of Ohmic regime to the limiting regime takes place.

The hydrogels were not compatible enough to handle the elevated NaCl-solutions. Besides, due to the low charge density of the hydrogel, probably ion transport could not take place selectively at high concentrations. If the efficiency could have been determined, then this explanation could be validated.

From the model can be concluded that flow rate and location of the investigated channel component have influence on the formation of depletion zones. The larger the depletion zones, the more ion exchange has taken place. Higher flow rates lead to less depletion zone formation, because higher flow rates promotes turbulence and so better mixing of ions occurs near the hydrogel surface. However, when the flow rate is set too high, ion exchange would not take place in a sufficient way. Across the entire channel, larger depletion zones were formed at the end of the channel.

Despite the goal of this research is not reached, more insight is obtained regarding the measurement set-up and methods. This knowledge can be used in further research to investigate the influence of higher concentrations of NaCl-solutions on a microfluidic device with the use of hydrogels.

6 Recommendations

The important recommendations of this research are divided in three main categories: the measurement equipment, the adaptions of the microfluidic device and recommendations for further long-term research.

1. Measurement equipment

The used methods to determine the efficiency parameters did not work for the experiments. A calibration curve could not be made, because of the large error in the measurement equipment in order to determine the conductivity. For further research, different tools should be used to determine the concentration more accurately. For example the equipment that is used in the article of Gumuscu *et al.* [1]. In this article, measurements were also performed at higher potentials, which was not possible with the used equipment in this research. Besides this, the off-set potential tool should be used in the IV-curve measurements, to ensure that the curve starts at (0,0). In this way, the curves will not be shifted.

2. Adaptions of microfluidic device

Liquid leakage and air bubble formation led to difficulties during the experiments. If this could be prevented by using other chips, the experiments could better be performed. Furthermore, if hydrogels could be made from other substances in such a way that the current density and the permselectivity of the hydrogels increases, experiments at higher concentrated NaCl-solutions could better be performed. Another possibility to work at higher concentrations and higher flow rates, is to use the same micro chip with an increased length of hydrogel stacks. When the length of the hydrogel stacks in the micro chip is increased, the total exchange area and therefore also the residence time will increase. This maybe can handle the higher concentrated solutions and ensures more ion exchange, which should have a positive effect on the salt removal efficiency. In this way, no need of a larger applied potential difference is needed. This micro chip was available in the lab, although it also gave some problems. In these experiments the larger shaped micro chip had even more liquid leakage problems near the in- and outlets and at the electrode inserts. Hence, it can be concluded that a micro chip with more hydrogels could work with higher concentrated solutions, provided that a solution could be found to discourage liquid leakage and air bubble formation.

3. Long-term research

When the microfluidic device works at the concentrations that are used in this assignment, the concentrations can be increased further in such a way that it is possible to use it when brackish water is used as feed. After this is reached, further research is worthwhile to look at other solutions. In this assignment only NaCl-solutions were used, nevertheless to come closer to real brackish water conditions, divalent ions play also an important role. Eventually, brackish water consists of a mixture of several ion concentrations. Taken into account that divalent ions have different behaviour than monovalent ions, a closer look should be taken to influences of different valences on the transport phenomena, like the ion concentration polarisation and so the formation of boundary layers.

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A | Appendix - Additional figures



Figure A.1: Average IV sweeps of different inlet concentrations with standard deviation error box, with a flow rate of 6 μ L/min.



Figure A.2: Dimensionless concentration profile over y-direction of channel component 5 including time dependency (applied potential is 2 V and the flow rate is 6μ L/min).