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Characterization of ion selective membranes for application in reverse electrodialysis systems

Concentration dependency of the apparent transport number

Robin Viktor Strand

Kjemi	
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Hovedveileder:	Signe Kjelstrup, IKJ
Medveileder:	Odne Burheim, IKJ Katrine Sandbakk, IKJ

Norges teknisk-naturvitenskapelige universitet
Institutt for kjemi

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Abstract

Reverse electrodialysis (RED) is a renewable, non-polluting way to generate electricity by mixing water with different salt concentration, e.g. river water and seawater. RED relies on ion selective membranes. Their efficiency can be described with their apparent transport number, which is the ratio between the measurable electromotive force (Emf) over the membrane and the ideal electric potential, which is regarded as the theoretical maximum. The apparent transport number is also referred to as the permselectivity. Here it is shown that the non-ideal behavior of an ion selective membrane, meaning it has an apparent transport number below 1 and that the apparent transport number goes down with increasing salt concentration, can be explained by electroosmosis. This is in contrast to the common interpretation that the apparent transport number is a measure of the membranes selectivity. The water transport number describes the direction and degree of the electroosmosis.

This interpretation is tested experimentally with Emf measurements of ion selective membranes at different concentrations. From the results it is shown that the anion selective membrane Fumasep FAD behaves as if it is perfectly selective and have a water transport number of -4.8±0.8 with saltwater solutions in the concentration range 2-30 grams sodium chloride (NaCl) per liter. Therefore, if manufacturers like Fumatech want to produce more efficient membranes there is no need to make them more selective against ions, but instead make them selective against water. It was also shown that the water transport could in special cases give apparent transport numbers greater than 1. This may help explain recent results published by Nature.

Effect of this model of the apparent transport number on the predicted performance of RED system was investigated using Matlab simulations. It is compared to how the apparent transport number is generally treated, namely as a constant that describes the membrane selectivity. The apparent transport number is calculated from Emf measurements and is dependent on the concentrations used under this measurement. It was found that the old approach is a good approximation at higher flow rates, with less than 1 % difference for flow rates above 1 mm/s. However, this is if the apparent transport number was measured at the concentrations at the inlets. If the apparent transport number is measured at different concentrations the difference will be larger. The predicted power output would be 7 % lower if the concentrations were 20 and 30 g/l NaCl instead of 3 and 30 g/l NaCl. In these simulations a water transport number of 10 was used. A higher water transport number would give a larger difference. The water transport number in ion selective membranes have been measured to be 4-50, but most commercial membranes do not have water transport numbers as high as 20-50.

Sammendrag

Revers elektrodialyse (RED) er en fornybar, ikke-forurensende måte å generere elektrisitet på ved å blande vann med forskjellige saltkonsentrasjoner, e.g. elvevann og sjøvann. RED er avhengig av ioneselektive membraner. Deres effektivitet kan bli beskrevet med deres effektive transporttall, som er ratioen mellom den målbare elektromotoriske kraften (Emf) over membranen og det ideelle potensialet, som er sett på som det teoretiske maksimum. Her er det vist at den ikke-ideelle oppførselen til en ioneselektiv membran, det at den har et effektivt transporttall under 1 og at det effektive transportallet går ned med økende saltkonsentrasjon, kan bli forklart med elektroosmose. Dette er i kontrast til den utbredte tolkningen at det effektive transporttallet er et mål på selektiviteten til membranen. Vanntransporttallet beskriver retningen og graden av elektroosmose.

Denne tolkningen er testet eksperimentelt med Emf målinger av ioneselektive membraner ved forskjellige konsentrasjoner. Fra resultatene er det vist at den anionselektive membranen Fumasep FAD oppfører seg som om den er helt selektiv og har et vanntransporttall på -4.8±0.8 med saltvannsløsninger i konsentrasjonsområdet 2-30 gram natriumklorid (NaCl) per liter. Derfor, hvis produsenter som Fumatech vil produsere mer effektive membraner trenger de ikke å gjøre membranene mer selektive ovenfor ioner, men istedenfor må de gjøre dem mer selektive ovenfor vann. Det er også vist teoretisk at vanntransporten i spesielle tilfeller kan gi transporttall over 1. Dette kan bidra til å forklare resultatene som nylig ble publisert av Nature.

Effekten av denne modellen av det effektive transporttallet på predikert ytelse av RED systemer ble undersøkt ved hjelp av Matlab simulasjoner. Det ble sammenliknet med hvordan det effektive transporttallet vanligvis er behandlet, det vil si som en konstant som beskriver selektiviteten av membranen. Det effektive transporttallet er regnet ut fra Emf målinger og avhenger av konsentrasjonen som blir brukt under denne målingen. Det ble funnet at den gamle metoden er en god approksimasjon ved høye strømningshastigheter, med under 1 % forskjell ved strømningshastigheter over 1 mm/s, hvis det effektive transporttallet er målt i konsentrasjonene ved innløpet. Hvis transporttallet er målt ved andre konsentrasjoner vil forskjellen være større. Den predikerte kraftproduksjonen vil være 7 % mindre hvis konsentrasjonene 20 og 30 g/l NaCl er brukt istedenfor 3 og 30 g/l NaCl. I disse simulasjonene et vanntransporttall på 10 var brukt. Et større vanntransporttall vil gi større

effekt. Vanntransporttallene til ioneselektive membraner har blitt målt til å være 4-50, men de fleste kommersielle membranene har ikke vanntransporttall så høye som 20-50.

Nomenclature

Greek or partially Greek symbols

α	Permselectivity of a membrane as defined by the literature	(-)
γ	Activity coefficient of NaCl	(-)
ΔG	Gibbs energy	(J/mol)
$\Delta\mathrm{x}$	Thickness of the membrane	(m)
$\Delta\mathrm{y}$	Width of the membrane	(m)
$\Delta\mathcal{X}$	Thickness of the water compartments	(m)
Λ_0	Molar conductivity at infinite dilution	($\Omega^{-1}m^{-1}$)
$Lambda_m$	Molar conductivity	($\Omega^{-1}m^{-1}$)
rho	Density of water	(kg/l)

Roman symbols

a	Activity of NaCl	(-)
A	Average number of water molecules each sodium ion drags with it	(-)
B	Average number of water molecules each chloride ion drags with it	(-)
C	Concentration of NaCl	(mol/l)
D	Diffusion coefficient	(m^2/s)
E	Measurable electric potential between the electrodes	(V)
E_{id}	Potential of an idealized membrane	(V)
E_{unit}	Measurable electric potential over a unit cell consisting of a cation and a anion selective membrane	(V)
F	Faradays constant	(C/mol)
F_o	Flow rate of ocean water	(mol/s)
F_r	Flow rate of river water	(mol/s)
j	Electric flux	(A/m^{2}s)
J_s	Flux of salt	(mol/m^{2}s)
J_w	Flux of water	(mol/m^{2}s)
k$_i$	A constant	(-)
L$_{ij}$	Phenomenological coefficients, Onsager coefficients	(-)
Lz	Length of RED system [m]	(m)
m	Concentration of NaCl	(mol/kg)
M_{H_2O}	Molar mass of water	(kg/mol)
m_o	Concentration of ocean water compartment	(mol/kg)
m_r	Concentration of river water compartment	(mol/kg)
R	The gas constant	(J/(mol K))
Res	Electrical resistance of cation selective membrane	(Ω m^2)
T	Temperature [K]	(K)
t_s	Transference coefficient of NaCl	(-)
t_{Na^+}	Transport number of sodium	(-)
t_{Cl^-}	Transport number of chloride	(-)
t_w	Transport number of water	(-)
t'	The apparent transport number (of sodium unless stated otherwise)	(-)
t'(m)	The apparent transport number at a given concentration	(-)
t'$_{Cl^-}$	The apparent transport number of chloride	(-)
t'(m1,m2)	The apparent transport number of a membrane separating two solutions of different concentration	(-)
x	Direction perpendicular to the membrane	(-)
y	Direction perpendicular to z and x	(-)
z	Direction of the flow	(-)

Contents

1 Introduction

1.1 Significance of saline power

Renewable energy sources are becoming more and more important as the amount of fossil fuel is shrinking and the use of it will cause more and more severe climate change. A relatively new form of renewable energy is salinity gradient power (SGP), also called blue power. This is the energy that can be generated by the reversible mixing of water with different salt concentrations. River and ocean water can therefore be used to generate electricity. The global potential can be calculated from multiplying the average potential energy density of river water and multiplying it by the total flow rate of all the worlds rivers. This potential is estimated to be 2.6-2.8 TW[4, 5]. In 2008, the average world energy consumption was 15 TW. 5 TW of this was used to generate 2 TW of electrical energy with low efficient coal fired power plants [5]. This is less than the global potential of SPG. Just the Rhine has a power potential of 3.9 GW, which is about 30 % of the electricity consumption in the Netherlands[2] where it runs out into the ocean.

1.2 Significance of the apparent transport number

There are different ways of converting this potential energy to electricity, the most known are pressure retarded osmosis and reverse electrodialysis (RED). Both are membrane-based technologies. In this project, membrane properties have been investigated in relation to RED. RED generally use a stack of cation and anion selective membranes. The amount of power one is able to extract is proportional to the apparent transport numbers of the membrane. The apparent transport number is the ratio between the measurable electric potential over the membrane and the theoretical maximum potential. This has been interpreted as a measure of ion selectivity of the ion selective membrane and is sometimes referred to as the permselectivity[6]. The selectivity of the membrane is the membranes ability to let ions of either positive or negative charge through while excluding ions of opposite charge. This is described with the transport numbers of the ions of the membrane. The transport number of an ion is the ratio of the amount of ions that travel through the membrane and the amount of electrons that travel between the electrodes. For a perfectly selective membrane this would be 1 for the ion it is selective for. The transport number is different from the apparent transport number, but by interpreting the apparent transport number as a measure of selectivity this is ignored. The electric resistance of the RED system and the apparent transport number limits the amount of power it is possible to extract per square meter of membrane. Manufactures are today able to make membranes with apparent transport numbers of around 0.9, values as high as 0.99 has been reported[7].

1.3 Main objective and outline of thesis

The apparent transport number is generally taken to be a constant, but it has been found that it tend to decrease with increasing concentration[8, 9, 10, 11, 12, 13]. This is generally interpreted as the membrane becoming less selective at higher concentrations. Another proposed explanation of the concentration dependency of the apparent transport number and its non-ideal value is that it is caused by electroosmosis, but not many papers have been written about it[9, 14, 15, 19]. Apparent transport number above 1 have not been reported, but an apparent transport number of 1.4 can be calculated for a boron nitride nanotube based on the results published in the supplementary information of a recent Nature article (see Ref. [1]). Since the apparent transport number changes it is not well described by a constant. A better description would be an equation. One equation that describes the apparent transport numbers dependency of the concentration has already been derived[14], but this deals only with a single concentration and does not take into account that when the apparent transport number is calculated from Emf measurements, which require the membrane to be in contact with two solution of different concentration. To get results from this equation one has therefore been using the average of the two concentration, which is an approximation. A more complete understanding of the apparent transport numbers could help manufacturers make membranes with higher transport numbers, which could then produce more electricity and make SGP a more viable option for power production. However, it should be noted that the main obstacle for SGP is not efficiency but membrane production cost[16].

An aim of this thesis is therefore to accurately describe the apparent transport number dependency on the electroosmosis and the two concentrations of the solutions that the membrane separates. The apparent transport number is investigated theoretically in Section 2 using irreversible thermodynamics. Here the apparent transport numbers dependency on the electroosmosis and the two concentrations are derived, resulting in several equations. Other effects of the water transport is also investigated.

In Section 3 the apparent transport numbers of an anion selective membrane, Fumasep FAD, and a cation selective membrane, Fumasep FKD, were investigated through Emf measurements. Here it was attempted to uncover which of the equations in Section 2 that best described the particular membrane and the value of its coefficients.

In Section 4 the effect of the findings from the previous sections on the predicted performance of a RED system is investigated using Matlab simulations. This is compared to how the apparent transport number is generally treated, namely as a constant describing the selectivity of the membrane.

The results from Sections 3 and 4 are discussed in Section 5 along with some previous findings from literature.

2 Theory

In this section, the concentration dependence of the apparent transport number is investigated using irreversible thermodynamics. The apparent transport number is the ratio between the measurable electric potential over the membrane and the ideal potential, which is considered the theoretical maximum. The concentration dependency caused by the water transport is derived in Section 2.1. How this can inhibit complete transfer of salt in a RED system is explored in Section 2.2 and its effect on desalination through electrodialysis is described in Section 2.3. The concentration dependency of the apparent transport number when the transport number themselves is dependent on the concentration is explored in Section 2.4. The theoretical possibility of apparent transport numbers above 1 is shown in Section 2.5. After that in Section 2.6 it is shown how the chemical potential was calculated.

2.1 Concentration dependency of the apparent transport number

In this section, the transport numbers of the ions and water is assumed constant and the concentration dependency caused by the water transport is derived. For a discussion of the concentration dependency of the apparent transport number when transport numbers are not constant see Section 2.4.

The force-flux relation for electric flux through an ion selective membrane is:

$$j = -L_{\phi s}\frac{d\mu_s}{dx} - L_{\phi w}\frac{d\mu_w}{dx} - L_{\phi\phi}\frac{dE}{dx} \tag{1}$$

Where j is the electric flux, μ_s is the chemical potential of sodium chloride (NaCl), μ_w is the chemical potential of water, L_{ij} are Onsager coefficients, E is the measurable electric potential and x is the direction perpendicular to the membrane.

For Emf measurements the electric flux is close to zero so Equation 1 becomes:

$$\frac{dE}{dx} = -\frac{L_{\phi s}}{L_{\phi\phi}}\frac{d\mu_s}{dx} - \frac{L_{\phi w}}{L_{\phi\phi}}\frac{d\mu_w}{dx} \tag{2}$$

The transference coefficient for NaCl is defined as:

$$t_s \equiv F\frac{L_{\phi s}}{L_{\phi\phi}} \tag{3}$$

t_s is the transference coefficient of NaCl and F is Faradays constant. If the electrodes used are reversible to chloride ions then the transference coefficient of NaCl, t_s, is interpreted to be the same as the transport number for sodium ions, t_{Na^+}.

The sum of the transport numbers of the ions are 1, and each of them are between 1 and 0.

$$t_{Na^+} + t_{Cl^-} = 1 \tag{4}$$

The transport number of water is:

$$t_w = F\frac{L_{\phi w}}{L_{\phi\phi}} \tag{5}$$

A model of how the transport number of water is related to the transport number of the ions are [17, 18]:

$$t_w = A * t_{Na^+} - B * t_{Cl^-} \tag{6}$$

Where A is the average number of water molecules each sodium ion drags with it through the membrane and B is the average number of water molecules each chloride ion drags with it through the membrane. The second term is negative since the chloride ions move in opposite direction to the sodium ions.

The chemical potential of water at constant temperature and pressure can be eliminated by using the Gibbs-Duhem equation:

$$C_s d\mu_s + C_w d\mu_w = 0 \tag{7}$$

$$d\mu_w = -\frac{C_s}{C_w}d\mu_s = -mM_{H_2O}d\mu_s \tag{8}$$

Where C_s is the concentration of the salt in mol/l, C_w is the concentration of water in mol/l, m is molal concentration of NaCl and M_{H_2O} is the molar mass of water in kg per mol.

If the Onsager coefficients are substituted with transport numbers and Gibbs-Duhem equation is used to eliminate the chemical potential of water Equation 2 becomes:

$$\frac{dE}{dx} = -\frac{1}{F}\left(t_{Na^+} - mM_{H_2O}t_w\right)\frac{d\mu_s}{dx} \tag{9}$$

If Equation 9 is integrated from one side of the membrane where the concentration of salt is m_1 to the other where the concentration is m_2 it becomes:

$$E = -\frac{1}{F}\int_{m_1}^{m_2} \left(t_{Na^+} - mM_{H_2O}t_w\right)\frac{d\mu_s}{dm}dm \tag{10}$$

The unit cell potential, the potential of the repeating unit in a RED stack, would be equal to the measurable potential over the cation selective membrane minus the potential over the anion selective membrane.

$$E_{unit} = -\frac{1}{F}\int_{m_1}^{m_2} \left(t_{Na^+}^{CM} - t_{Na^+}^{AM} - mM_{H_2O}(t_w^{CM} - t_w^{AM})\right)\frac{d\mu_s}{dm}dm \tag{11}$$

Where the superscript CM means the transport number belong to the cation selective membrane and AM means anion selective membrane. The water transport number in the anion selective membrane tends to be of the opposite sign as the transport number of water in the cation selective membrane, since the ions move in opposite directions. This could also be written as:

$$E_{unit} = -\frac{1}{F}(t_{Na^+}^{CM} - t_{Na^+})\Delta\mu_s - \frac{1}{F}(t_w^{CM} - t_w^{AM})\Delta\mu_w \tag{12}$$

The apparent transport number is found by dividing the measured Emf by the ideal Emf.

$$t' = \frac{E}{E_{id}} \tag{13}$$

The ideal potential is defined as:

$$E_{id} = -\frac{\Delta\mu_s}{F} \tag{14}$$

This is what the measured potential would be if the transport number of sodium where 1 and the transport number of water where 0.

So the expression for the apparent transport number becomes:

$$t' = \frac{\int_{m_1}^{m_2}\left(t_{Na^+} - mM_{H_2O}t_w\right)\frac{d\mu_s}{dm}dm}{\Delta\mu_s} \tag{15}$$

If the transport numbers does not change with the concentration, it becomes:

$$t' = t_{Na^+} - \frac{M_{H_2O}t_w\int_{m_1}^{m_2} m\frac{d\mu_s}{dm}dm}{\Delta\mu_s} \tag{16}$$

Where $\Delta\mu_s = \mu_s(m_2) - \mu_s(m_1)$.

The apparent transport number in Equation 15 is what is measured through experiments. This depends on the concentrations on both sides of the membrane, t'=t'(m_1, m_2). The experiments in the later sections have tried to determine the concentration dependency of t', t'(m), where the concentration is the same on both sides of the membrane. From Equation 15 how the t'(m) can be found by having $\Delta\mu_s$ go to $d\mu_s$.

$$t'(m) = t_{Na^+} - mM_{H_2O}t_w \tag{17}$$

t'(m) is a theoretical coefficient and cannot be measured directly, at least not with Emf measurements. This equation have been reported before[14, 19, 15] where it was derived from the Scatchard equation. t'(m) is related to t'(m_1, m_2) by this equation:

$$t'(m_1, m_2) = \frac{\int_{m_1}^{m_2} t'(m) d\mu_s}{\Delta\mu_s} \tag{18}$$

In addition, the electric potential by this equation:

$$E = \int_{m_1}^{m_2} t'(m) d\mu_s \tag{19}$$

How the apparent transport number depends on the two concentrations is illustrated in Figure 1 below. Here it has been assumed that the transport numbers do not depend on the concentration and have been set to 1 and 10 for sodium and water. The figure is not only valid for cation selective membranes. One would get the same result for the apparent transport number of chloride of an anion exchange membrane, if the transport numbers of sodium and water were set to 0 and -10. The water transport number is negative for anion selective membranes, since the water molecules are carried by the chloride ions which move in the opposite direction to the sodium ions.

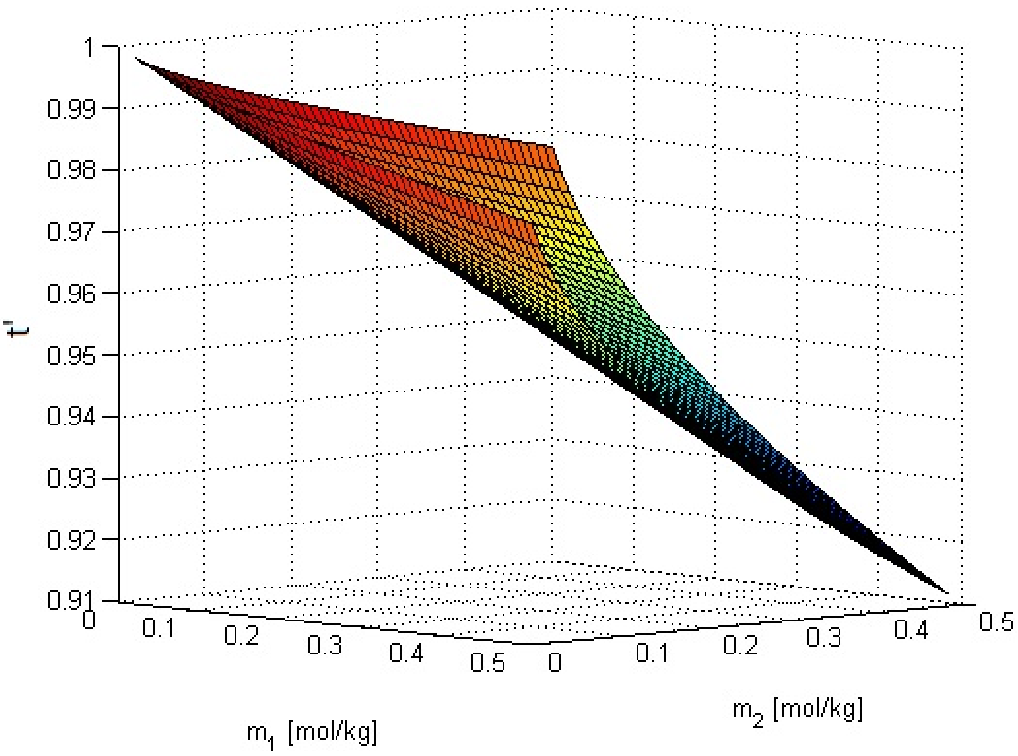

Figure 1: The apparent transport number and the two concentrations.

The apparent transport number is highest when both concentrations are low and lowest when both concentrations are high. The diagonal is described by Equation 17. The same results are shown again in Figure 2.

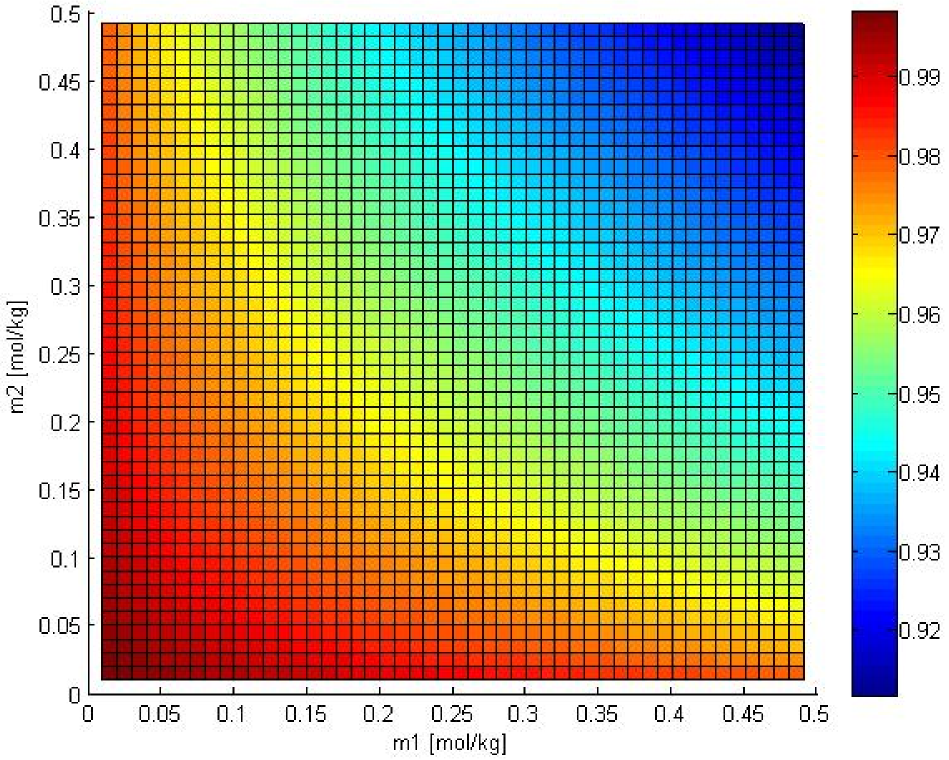

Figure 2: The apparent transport number and the two concentrations.

Figure 2 is the same as Figure 1, but here the value of the apparent transport number is indicated by color only. The figure is symmetric. The value increases to the left and down. This means that if the larger concentration is kept constant the apparent transport number increases with increasing concentration difference. This is shown in Figure 3 below where the constant concentration is kept at 0.5 mol/kg.

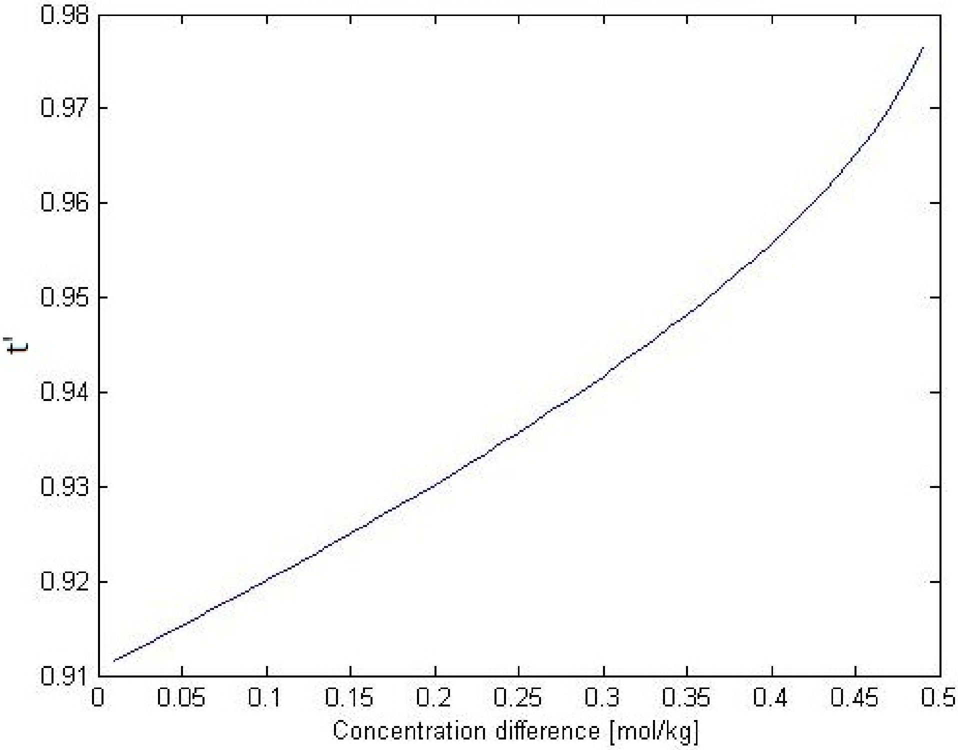

Figure 3: How the apparent transport number changes with concentration difference if the largest concentration is kept constant.

The apparent transport number is clearly increasing. The figures 1-3 can be explained by the Gibbs energy of the reaction and the Nernst equation. The Nernst equation for monovalent ions is:

$$E = -\frac{\Delta G}{F} \tag{20}$$

Where ΔG is the Gibbs energy of the reaction accompanied by the transfer of 1 mol electrons from one electrode to the other. Let us first look at the cation exchange membrane. The salt is transferred from the concentrated solution to the more diluted solution. The water is transferred with it from concentrated to dilute. The transfer of the salt equalizes the concentrations and therefore have a negative Gibbs energy. The transfer of water counteracts this by making the concentrated solution more concentrated and diluting the diluted solution. The Gibbs energy of this is therefore positive and lowers the absolute value of the overall Gibbs energy of the reaction. This gives a lower electric potential and apparent transport number. The effect of the water transfer is higher for more concentrated solutions because the ratio between the amount of salt and water is lower, so the same amount of water transfer will change this ratio (and the concentration) more and therefore be more efficient at counteracting the equalizing of the concentrations. That is why increasing the concentrations of either solution will give a lower apparent transport number of sodium. This is if the membrane is a cation exchange membrane and the transport numbers do not depend on the concentration and the water transport number is non-zero.

For anion exchange membranes it is different. The transport number of chloride is close to 1, while the transport number of sodium is close to zero. The chloride ions move in the opposite direction to the sodium ions from the diluted side to the concentrated. The water is dragged along so the water transport is also from the diluted to the concentrated. Since the electrodes are reversible to the chloride ions the transfer of chloride does not change the concentration. The Gibbs energy of this is therefore zero. The water transport on the other hand equalized the concentrations. Therefore the Gibbs energy of this is negative. This gives an electric potential (Equation 20) and increases the apparent transport number of sodium (Equation 13). This lowers the apparent transport number of chloride which is 1-t'. In a cell stack, the electric potential created by the water transport will be in the opposite direction as the potential over the cation selective membrane, so it will make the cell stack less effective just as the water transport through the cation selective membrane will. To make ion selective membranes that perform better one should therefore make them selective against water so that they have a water transport number as close to zero as possible.

The apparent transport number would still be a function of the concentrations on both sides of the membrane if there was no water transport across the membrane and the selectivity decreased with concentration[20], but the nature of the concentration dependency would be different. One might think that only the highest concentration would matter since for example the transport number of the cation in a cation selective membrane would be lowest in the part of the membrane that was in contact with the solution of the highest concentration. One might think that this would limit the transport of cation through the membrane working as a bottleneck for the cation. The transport number of cation for the entire membrane would therefore be the transport number of cation of the membrane at the highest concentration. This is incorrect because the other ion, here anion, has been ignored. The sum of transport numbers of the ions over the entire membrane is 1, so they are dependent on each other. The transport number of the anion would here be lowest at the lowest concentration so this would limit the transport of anions and the bottleneck dependent on the lowest concentration. Therefore the apparent transport number is a function of both concentrations.

It has also been argued that if the transport number of the ions depend on the concentration the transport number of the entire membrane would be equal to the transport number at the concentration of the solution receiving the ions[13]. This goes against what is stated in Ref. [20] and what you get from irreversible thermodynamics, but the equations from irreversible thermodynamics is dependent on local equilibrium between the membrane and the solutions. The argument for this concentration dependency is that the difference in the transport numbers on the two sides of the membrane will lead to a build up of electrolytes in the membrane so the entire membrane is in exchange equilibrium with the solution receiving the ions and not the other solution. This should not effect the measurements done here because they are Emf measurements where there is no current between the electrodes and therefore no transport of ions through the membrane or buildup of electrolytes caused by this.

2.2 Inhibition of complete mixing caused by the water transport

If the water transport number is high enough it could hinder the concentration from ever equalizing over a cation selective membrane. This is illustrated in Figure 4 below.

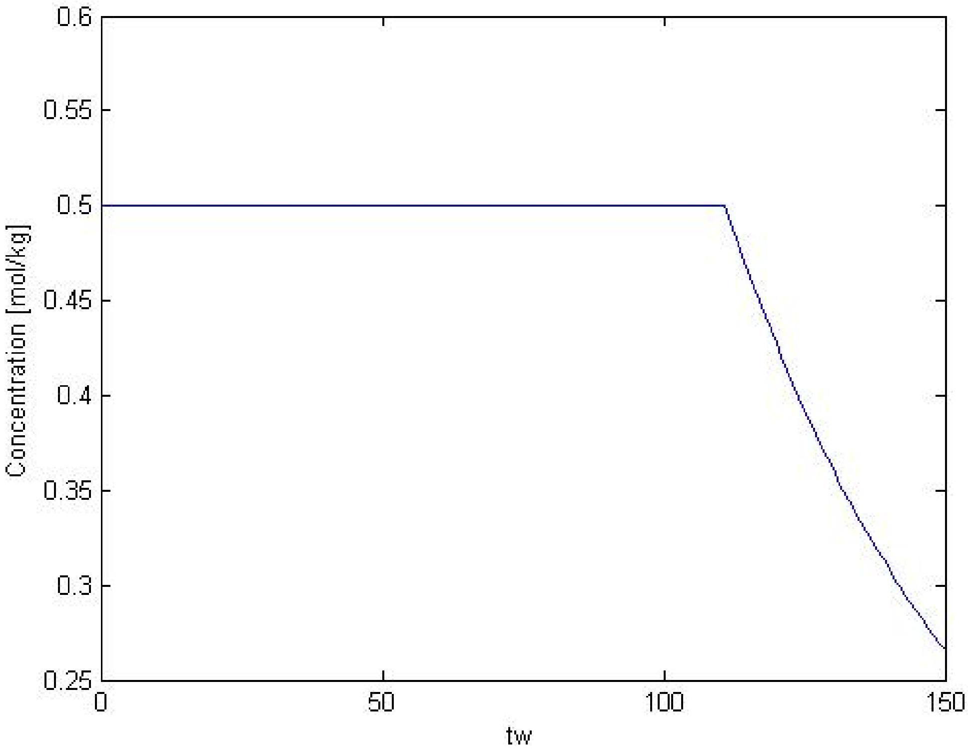

Figure 4: The concentration at which the electric potential is zero as a function of the water transport number if the other concentration is kept at 0.5 mol/kg.

The results in Figure 4 is calculated from Equation 16. The transport number of sodium was set to 1. One concentration was set to 0.5 mol/kg and then the other was found under that condition that t'=0. If the transport number of water is low the concentration at which is t' or E is zero is the same as the concentration of the other solution, but if it is high enough the electric potential over the membrane will be zero even if there is a concentration difference. The same thing is shown again in Figure 5, but here the constant concentration is 0.25 mol/kg.

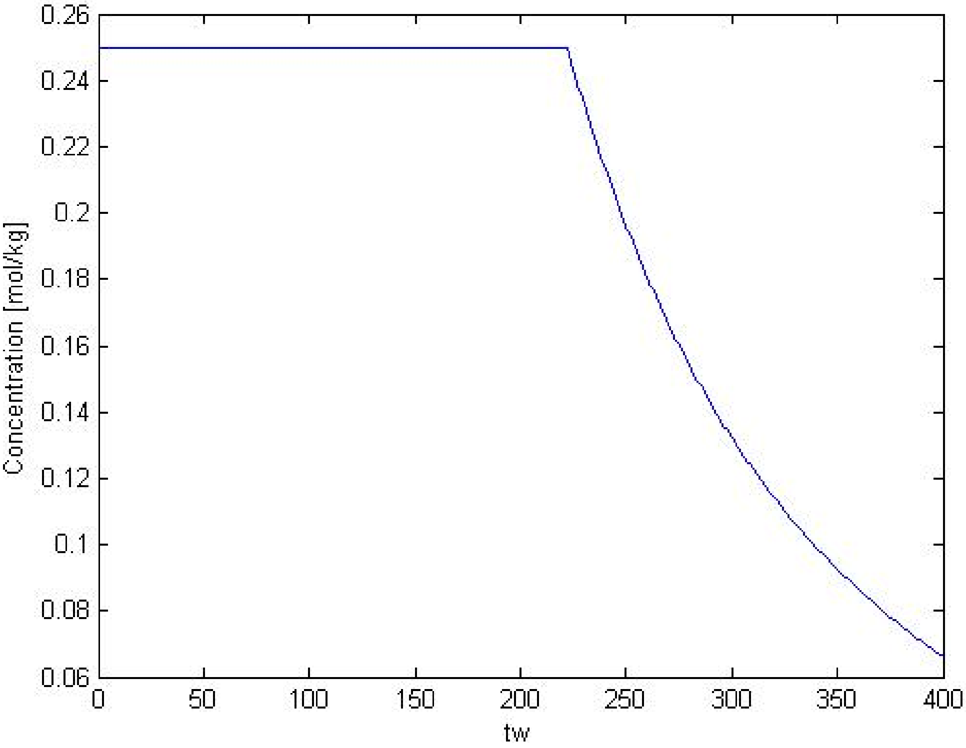

Figure 5: The concentration at which the electric potential is zero as a function of the water transport number if the other concentration is kept at 0.25 mol/kg.

For this lower concentration, the transport number of water must be higher to have the same effect. Hence the point in the graph where the function starts to go down is dependent on the concentration which has been kept constant. This dependency is shown in Figure 6.

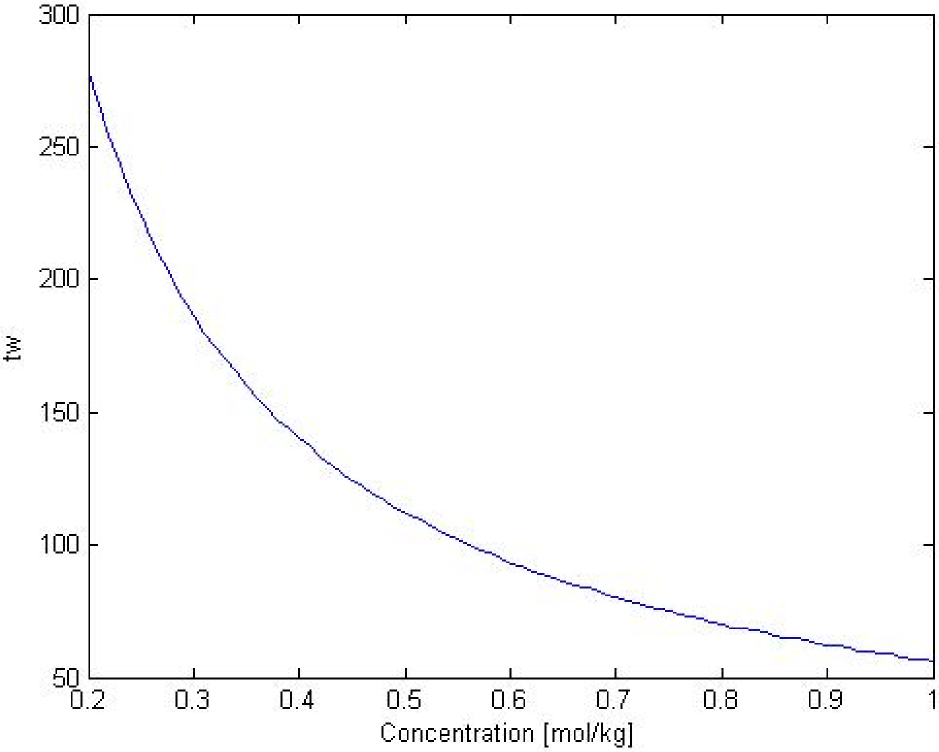

Figure 6: The transport number of water at which the electric potential is zero at a concentration difference of at least 1 % as a function of the concentration.

Figure 6 shows the transport number of water which gives an electric potential of zero even if there is a concentration gradient over the membrane. The concentrations of the solutions are on one side of the cation selective membrane given by the x-axis, the concentration on the other is 1 % less. The water transport number calculated is that which gives an electric potential over the membrane equal to zero. The transport numbers of water in Figure 6 is quite high, the transport number of water have been measured to be around 4-50 in ion selective membranes[2, 3].

2.3 Effect of water transport on desalination

The water transport also affects electrodialysis, which is used for desalination. Desalination of saltwater is used to produce drinking water or salt. Since for every t_{Na^+} mol salt that is transferred from one solution to another brings with it t$_w$ mol water there is a limit on how much you can increase the concentration of a solution if a cation selective membrane is used. The max concentration is given by Equation 21.

$$m_{max} = \frac{t_{Na^+}}{t_w M_{H_2O}} \tag{21}$$

Where m$_{max}$ is the maximum concentration of salt in mol/kg.

When salt is transported, water is transported with it. m$_{max}$ describes transferred amount salt in mol per transferred amount water in kg. Effectively this means that during desalination some amount of a solution with concentration m$_{max}$ is subtracted from one solution and added to the other, which can therefore not reach a concentration higher than m$_{max}$. There is however no limit of how diluted one could make the other solution.

What one could do instead of using a cation selective membrane is to use an anion selective membrane. The chloride ions could drag water from the concentrated solution to the diluted solution. The transport of chloride ions would not cause a transfer of salt, if electrodes reversible to chloride ions were used. With an anion selective membrane there would not be limit on how concentrated you could make a solution through electrodialysis. Nevertheless, there would be a limit on how diluted one could make the other solution. The minimum concentration is given by Equation 22.

$$m_{min} = \frac{t_{Na^+}}{|t_w| M_{H_2O}} \tag{22}$$

Where m$_{min}$ is the minimum concentration of salt in mol/kg. Since this is an anion selective membrane t_{Na^+} would be close to 0. The water transport number is negative for anion selective membranes, so the absolute value is used.

Using a stack of cation and anion selective membranes are similar to using a cation selective membrane in that salt and water is transferred from the concentrated side to the diluted side. There would therefore be a maximum possible concentration and no minimum like when only a cation selective membrane is used. The difference is that both chloride and sodium ions would transfer water. The maximum concentration is given by Equation .

$$m_{max} = \frac{t_{Na^+}}{(t_w^{CM} + |t_w^{AM}|) M_{H_2O}} \tag{23}$$

t_w^{CM} is the transport number of water in the cation selective membrane and t_w^{AM} is the transport number of water in the anion selective membrane. t_w^{AM} is negative since the water is transported in the opposite direction than in the cation selective membrane, because the positive and negative ions move in opposite direction. The absolute value of t_w^{AM} is the amount of water transferred through the anion selective membrane from the diluted solution to the concentrated.

2.4 Variable transport numbers

In the previous sections, the transport numbers of ions and water have been considered constant and do not change with the concentration. What if the transport numbers do change with the concentration? That the apparent transport number decreases with concentration, has traditionally been interpreted as the membrane becoming less selective. This could happen since increased concentration gives decreased Debye length of the charges of the charged groups in the membrane. The Debye length is a measure on how long into the solution a charge is felt by other charges in the solution. Ions of opposite charge will be attracted to the charges in the membrane and shield the other ions from their influence. The more ions there are in the solution the more the charges will be shielded and the shorter the Debye length. How would this affect the apparent transport number? Instead of being constant, let us instead assume the transport number of sodium in a cation selective membrane decrease linearly with the concentration.

$$t_{Na^+} = 1 - km \tag{24}$$

Where k is a positive constant with the dimensions kg/mol. This approximation is not valid for large concentrations since the transport number cannot be negative. At large concentrations, the Debye length would go to zero and the transport number in the membrane would go to value of the transport number in water.
Combining Equation 6 and 4:

$$t_w = (A + B)t_{Na^+} - B \tag{25}$$

Then combining Equation 25 and 24:

$$t_w = A - (A + B)km \tag{26}$$

Equation 24 and 26 can then be introduced into Equation 17:

$$t'(m) = 1 - km - mM_{H_2O}(A - (A + B)km) \tag{27}$$

$$t'(m) = 1 - (M_{H_2O}A + k)m + M_{H_2O}(A + B)km^2 \tag{28}$$

There is a similar equation for anion exchange membranes:

$$t'_{Cl^-}(m) = 1 - t'(m) = 1 - (M_{H_2O}B + k)m + M_{H_2O}(A + B)km^2 \tag{29}$$

Here t'$_{Cl^-}$(m) is the apparent transport number of chloride not sodium. The expression use here is t$_{Na^+}$ =km

Equation 29 and 27 are both of second order. Both of them predict a minimum.

2.4.1 Other concentrations dependencies

t$_{Na^+}$(m) in reality does not look like Equation 24, since it at some point flatten out as the concentration increases. In reality, it is unknown. Does this mean the predictions in the section above is invalid? There are many possible functions for t$_{Na^+}$(m). What is known is that it decreases with concentration and goes towards the value it has in water at large concentrations. Below is a couple of equations that fulfills these criteria and start of their Taylor expansion which is infinitely long for these equations. Any function can be written as a Taylor expansion. One could get an approximation of the function by including a couple of the first terms in the Taylor expansion. The number of terms included is proportional to the length of the interval where the approximation is approximately correct.

$$t_{Na^+} = k_1 + k_2 e^{-k_3 m} \tag{30}$$

$$t_{Na^+} = k_1 + k_2 * (1 - \frac{k_3 x}{1!} + \frac{k_3^2 x^2}{2!} - \frac{k_3^2 x^3}{3!} + ...) \tag{31}$$

Where k$_1$, k$_2$ and k$_3$ are constants. The signs of the terms alternate between positive and negative.

$$t_{Na^+} = k_1 + \frac{k_2}{m + k_3} \tag{32}$$

$$t_{Na^+} = k_1 + k_2(\frac{1}{k_3} - \frac{x}{k_3^2} + \frac{x^2}{k_3^3} - \frac{x^3}{k_3^4}...) \tag{33}$$

Where k$_1$, k$_2$ and k$_3$ are constants. The signs of the terms also alternate between positive and negative here.

Equation 24 could be an approximation of any decreasing function, since that is what one would get if only the two first terms of the Taylor expansion were included. What would Equation 29 and 27 look like if more terms were included? t'(m) is a polynomial of one order higher than t$_{Na^+}$(m), if t$_{Na^+}$(m) is a polynomial. Let us assume t$_{Na^+}$(m) looks like Equation 30 or 32. t'(m) would then have terms with alternating signs, where the constant would be positive, the second term negative, third positive and so on.

2.5 Apparent transport numbers greater than 1

Are apparent transport numbers larger than 1 possible? Using Equation 6 and 17 we get:

$$t'(m) = t_{Na^+} - mM_{H_2O}(At_{Na^+} - Bt_{Cl^-}) \tag{34}$$

$$t'(m) = t_{Na^+} - mM_{H_2O}At_{Na^+} + mM_{H_2O}Bt_{Cl^-}) \tag{35}$$

The third term describes the water transported by the chloride ion. It transport water from the diluted side to the concentrated side increasing the absolute value of the Gibbs energy of the reaction. This is why Equation 27 and 29 have a minimum, because in that case increasing the concentration lead to an increase in the transport number of chloride and therefore also water transport from the diluted side to the concentrated.

If the value of B is large enough it is theoretically possible to have an apparent transport number larger than 1. A and B are as mentioned the average number of water molecules transported by the sodium and chloride ions. They each have two contributions[18]: the water molecules bound to the ion and the water pumped by the ion during the ion transport process. The pumping is caused by the hydrated ions pushing water ahead of them and dragging them along behind them. The motion of the ions therefore creates a water current from one side of the membrane to the other. In membranes with a higher water content, the ions will pump more water. The ideal potential as defined in Equation 14 is therefore not actually the theoretical maximum because it ignores the transport of water.

As mentioned before to make better performing membranes one should make them selective against water so that their water transport number is as close to zero as possible. That is only if the water is mainly transported by the ion the membrane is selective for, meaning a positive water transport number for the cation selective membrane and a negative for the anion selective membrane. In special cases where the membrane is not perfectly selective and the ion the membrane is selective against transports far more water than the other ion this is not the case. This would be for example a cation selective membrane with a negative water transport number, where the water is mainly transported by the chloride. The other case would be an anion selective membrane with a positive water transport number, where the water is mainly transported cation. In these cases, the water transport would improve the apparent transport number and the performance of the membrane.

2.6 Chemical potential

The chemical potential of a solution of NaCl is:

$$\mu - \mu_0 = RTlog(a) = RTlog((\gamma * C)^2) = 2RTlog(\gamma * C) \tag{36}$$

Where μ is the chemical potential, μ_0 is standard chemical potential, R is the gas constant, T is the temperature, a is the activity, γ is the geometric average of activity coefficients of chloride and sodium and C is the concentration of NaCl in mol/l.

Table 1 shows how the activity coefficient depends on the concentration [21]. This is at 25 degrees Celsius.

Table 1: The activity coefficient, γ, at different concentrations.

C [mol/l]	γ
0.001	0.965
0.002	0.952
0.005	0.928
0.01	0.903
0.02	0.872
0.05	0.822
0.1	0.779
0.2	0.734
0.3	0.71
0.4	0.693
0.5	0.681
0.6	0.673
0.7	0.667
0.8	0.662
0.9	0.659
1	0.657

Figure 7 shows how the activity coefficient times the concentration in mol/l varies with the concentration in mol/kg.

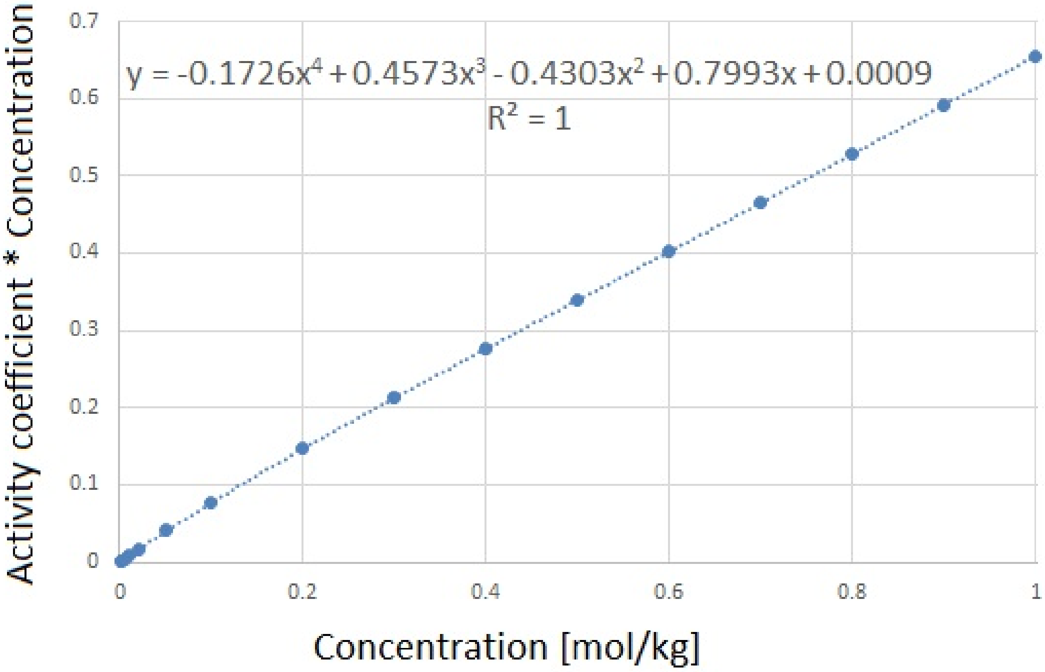

Figure 7: How the activity coefficient times the concentration changes with the concentration.

Based on the data in Table 1 a soft model was made of the chemical potential as shown by the equation in Figure 7. The uncertainty of the predictions from this model is shown in Table 2.

Table 2: The uncertainty in the predicted value at different concentrations.

m [mol/kg]	Two standard deviations [%]
0.001	160
0.002	80
0.005	30
0.01	16
0.02	8
0.05	4
0.1	2
0.2	1
0.3	0.7
0.4	0.6
0.5	0.5
0.6	0.4
0.7	0.3
0.8	0.3
0.9	0.3
1	0.3

The model is less accurate at lower concentrations and not valid for concentrations above 1 mol/l. The concentrations used in the experiments do not go below 0.03 and not above 0.6 so it should be fairly accurate.

3 Experiments

This section is about the measurements of Emf over ion selective membranes. The goal of the measurements was to determine how the apparent transport number of selective membranes changed as a function of the concentration. In other words to find the function t'(m) in Equation 17. The experiments were done with an anion selective membrane, namely Fumasep FAD, and a cation selective membrane, namely Fumasep FKD.

3.1 Experimental setup

The experimental setup is shown in Figure 8 below:

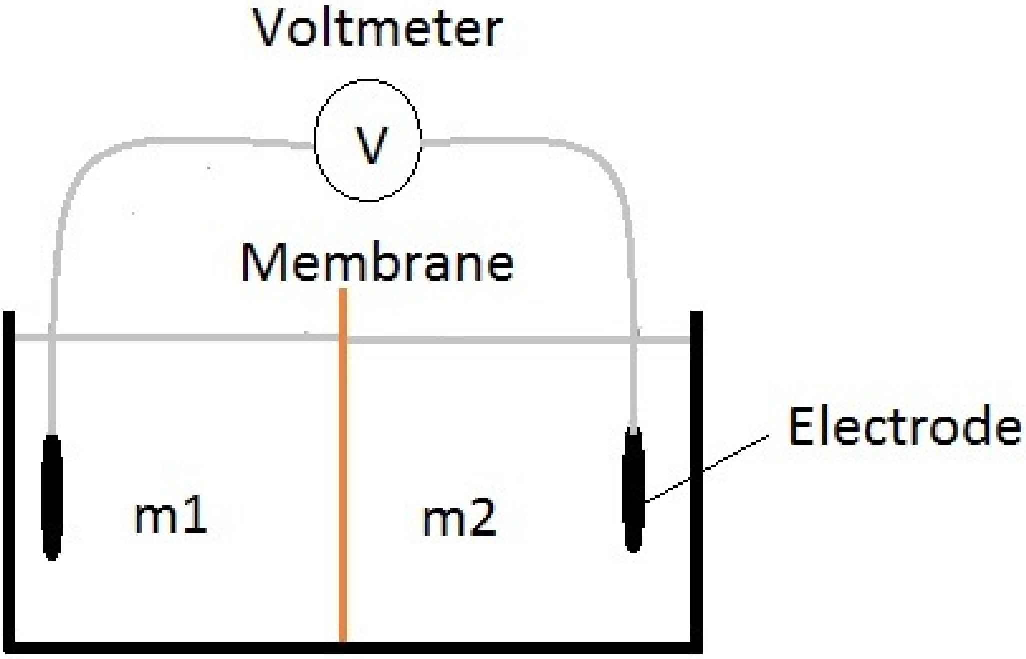

Figure 8: The experimental setup for the measurements.

Two saline solutions of concentration m_1 and m_2 are separated by the membrane in question. The electric potential over the membrane is measured. The concentration range investigated is between ca. 2g/l and ca. 30 g/l NaCl. To determine the apparent transport number at a given concentration there were done three or more measurements of electric potential, E, with the chosen concentration and a slightly higher concentration and three or more with a slightly lower concentration. The concentration were made with 0.1 % accuracy. The bias potential of the electrodes was measured in both solutions typically between 10^{-4} and 10^{-5} V. This bias was corrected for by subtracting the average of these two measurements from the measured electric potential. This corrected measurement will from now on be referred to as the measured electric potential. The bias potential is caused by differences in the electrode surface and change between each experiment. Since the bias potential might not be the exact average and might change during the experiment it is a cause of uncertainty in the measurements. This will matter more for the measurements of the potential over the anion membrane where the measurable potential is much lower and the bias potential therefore relatively larger.

16 membranes were used in each experiment, 8 that had been stored in one solution and 8 that had been stored in the other. The membranes were in contact with the solution they had been stored in. The reason so many membranes were used is that it slows down diffusion of salt and water through the membranes, which would affect the measurements. When a new experimental series started with new concentrations, the membranes were stored in the solution for at least 48 hours beforehand. They were not always stored in the solution between individual measurements. The membranes were stored at room temperature.

Two round-bottom flasks were used. They had a piece cut off on the side so they had a round hole of equal size. A rubber ring was place on the edge of each hole to protect the membranes. The diameter of these holes 4.3 cm. The membranes were placed on the rubber rings and the flasks were pushed and held together by an adjustable frame. The membranes were cut into rings with a diameter of 5 cm. Due to the rubber ring only an area with diameter of 3.5 cm of the membrane was exposed to the solutions. The two solutions were placed in the flasks. In the solutions there were placed magnet stirrers to avoid concentration polarization. The whole setup was placed in a water bath with a temperature of 25 degrees Celsius for the duration of the experiment. The membranes were wrapped in plastic wrapping to keep it from coming into contact with the water in the water bath. This setup were disassembled and reassembled between each measurement.

The membranes were not wiped of before use. This should not matter as long as there is a local equilibrium at the membrane-solution boundary between the two solutions and the membranes they touch. The concentration between the other membranes should not matter. The potential over a membrane is given by Equation 19 and can be written as:

$$E = f(m_2) - f(m_1) \tag{37}$$

Where f(m) is a function of the concentration and m_1 and m_2 is the concentrations on either side of the membrane.

Imagine there is a solution with different concentration between the two solutions, separated from the other solutions by a membrane. This is illustrated in Figure 9.

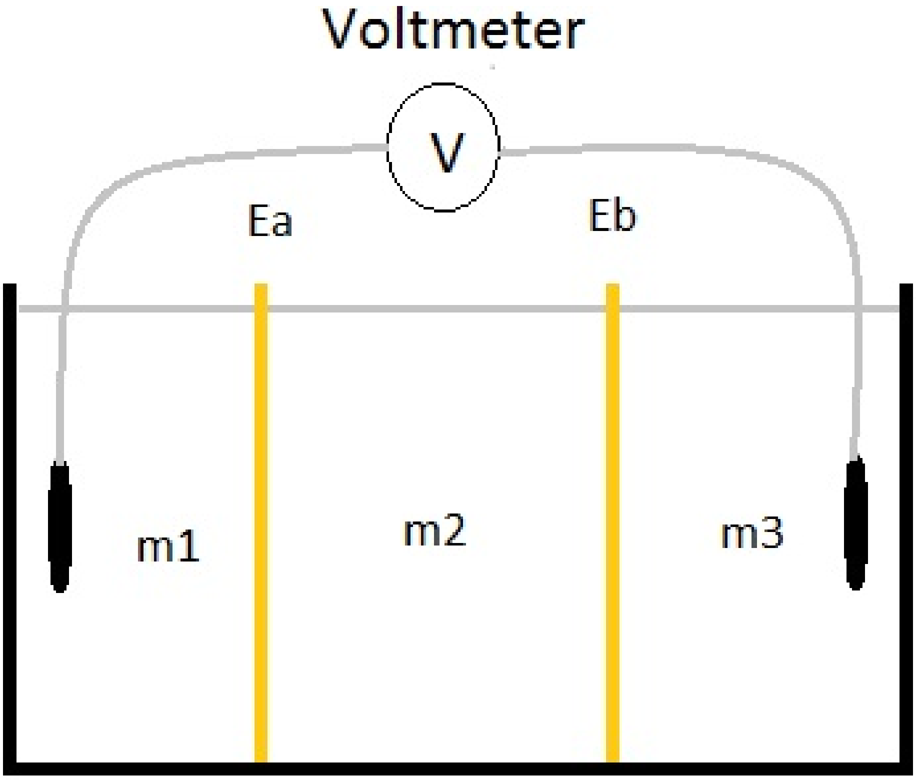

Figure 9: Illustration of hypothetical experiment in discussion.

There is potential over the membrane separating Solution 1 and 2 called E$_a$.

$$E_a = f(m_2) - f(m_1) \tag{38}$$

There is also a potential over the membrane separating Solution 2 and 3 called E$_b$.

$$E_b = f(m_3) - f(m_2) \tag{39}$$

The potential between Solution 1 and 3 is the sum of these potentials.

$$E_{tot} = E_a + E_b = f(m_2) - f(m_1) + f(m_3) - f(m_2) = f(m_3) - f(m1) \tag{40}$$

Where E$_{tot}$ is the potential between Solution 1 and 3. The concentration of the solution in the middle does not affect E$_{tot}$, hence the concentration of the solutions between the 16 membranes should not matter.

3.2 Finding t'(m) by assuming it is constant in a concentration range

The apparent transport number could then be found with Equation 13 and one would get t'(m) if it is assumed that the apparent transport number is constant over the concentration range used in each experiment. There is an error associated with this assumption. To reduce this error the concentration differences should be as small as possible. But smaller concentration differences give smaller E. If E is small then the noise in the measurements of E will get large compared to the signal. The concentrations where therefore selected to give an expected E of around 400 μv for the anion selective membrane and around 4000 μv for the cation selective membrane.

E should then be high enough for the uncertainty to not be a problem while still low enough that the concentration difference would not be too large. The apparent transport number of sodium of the anion selective membrane was found to be around 0.02 for low concentrations (under 0.2 molal) and around 0.05 for higher concentrations after some initial experiments. It was assumed to be around 1 for the cation selective membrane.

3.3 Finding t' with multiple linear regression

One could also calculate t' without making the assumption that it is constant over a concentration range. Hence future experiments does not require that low concentration difference which means the uncertainty in E, and subsequently t', could be lowered. Instead t' could be assumed to be a given function of the molality of NaCl:

$$t' = \sum_i C_i m^i \tag{41}$$

Where C_i are unknown coefficients and m is the molal concentration of NaCl. Put Equation 41 into Equation 19 and it becomes:

$$E = \int_{m_1}^{m_2} \sum_i C_i m^i d\mu_s \tag{42}$$

$$E = \sum_i C_i \int_{m_1}^{m_2} m^i \frac{d\mu_s}{dm} dm \tag{43}$$

Equation 43 can be written as:

$$E = \sum_i C_i x_i \tag{44}$$

Where C_i is unknown coefficients and x_i is variables. The x_i variables can be calculated if $\mu_s(m)$ is known. It was assumed that there is an exchange equilibrium between the membrane and the solution, therefore $\mu_s(m)$ is the same in the membrane as in a saline solution. The coefficients C_i could then be found by multiple linear regression.

If they are known then t'(m) is known. How many and which terms to include in Equation 17 and 43 must be decided before the calculations. The two methods is therefore synergistic. One could find the shape of t'(m) by assuming t' is constant over a concentration range, then from this shape decide how many terms to include in the multiple linear regression method.

3.4 Results for the anion selective membrane

3.4.1 Data

Table 3 below shows the concentrations used in each experiment and the measured electric potential. The experiments are divided into groups where each group has the same concentration combination. There are eight groups overall.

Table 3: The concentrations used and the measured potential

m_1 [mol/kg]	m_2 [mol/kg]	E [V]
Group 1		
0.05	0.03	-0.00010
0.05	0.03	-0.00025
0.05	0.03	-0.00001
0.05	0.03	-0.00019
0.05	0.03	-0.00002
Group 2		
0.05	0.09	0.00024
0.05	0.09	0.00015
0.05	0.09	0.00010
0.05	0.09	0.00008
Group 3		
0.17	0.09	-0.00046
0.17	0.09	-0.00026
0.17	0.09	-0.00025
Group 4		
0.17	0.32	0.00023
0.17	0.32	0.00031
0.17	0.32	0.00030
Group 5		
0.39	0.32	-0.00033
0.39	0.32	-0.00048
0.39	0.32	-0.00056
Group 6		
0.39	0.47	0.00029
0.39	0.47	0.00033
0.39	0.47	0.00048
Group 7		
0.5	0.39	-0.00065
0.5	0.39	-0.00054
0.5	0.39	-0.00057
Group 8		
0.5	0.6	0.00041
0.5	0.6	0.00055
0.5	0.6	0.00062

3.4.2 Results from assuming t' is constant in a concentration range

There are several ways to process the data in Table 3. The groups can be divided into pares where they share one concentration. One could assume t' is constant over the concentration range used in the two groups and say this is the apparent transport number for the concentration they have in common. The apparent transport number of Cl^-, which is 1-t', calculated this way is shown in Figure 10.

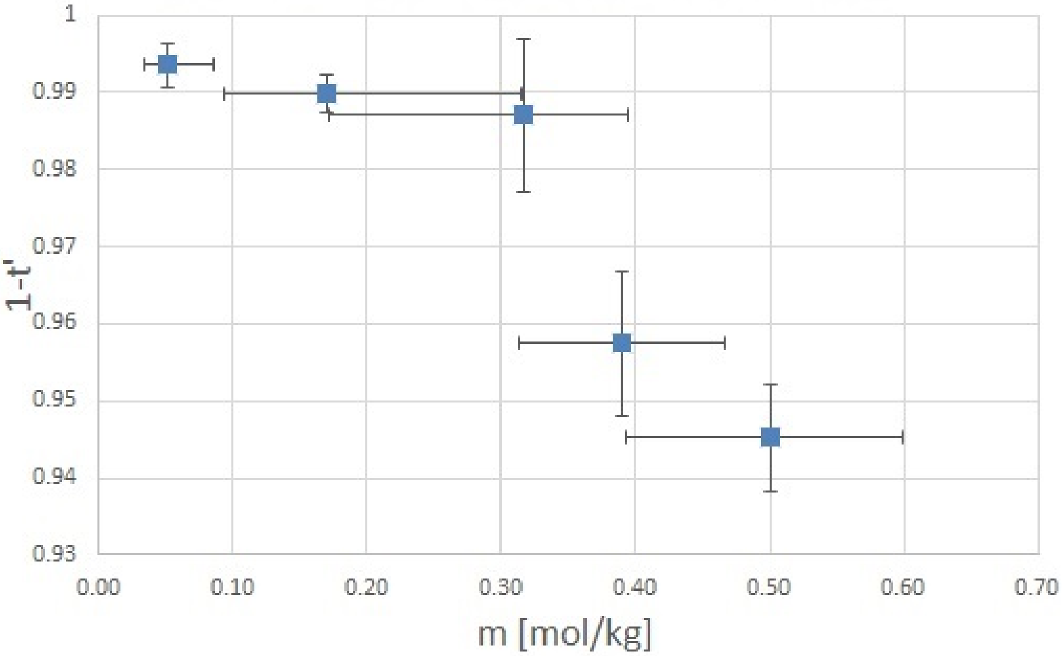

Figure 10: The apparent transport number of Cl^- as a function of the concentration of NaCl.

The figure shows how the apparent transport number, as calculated assuming t' is constant in a concentration interval, changes with the salt concentration. The results from two groups is used to calculate one point, which is placed at the concentration the two groups have in common. The horizontal error bars shows the concentration range that t' have been assumed to be constant in. The vertical error bars is caused by the uncertainty in the measured electric potential and represent two standard deviations. The uncertainty caused by the assumption that t' is constant is not accounted for.

There seem to be a downwards trend which means the membrane becomes less selective at higher concentrations. The concentration range that t' is assumed to be constant in, can be made smaller by using the results from only one group per point. The results for this procedure is shown in Figure 11

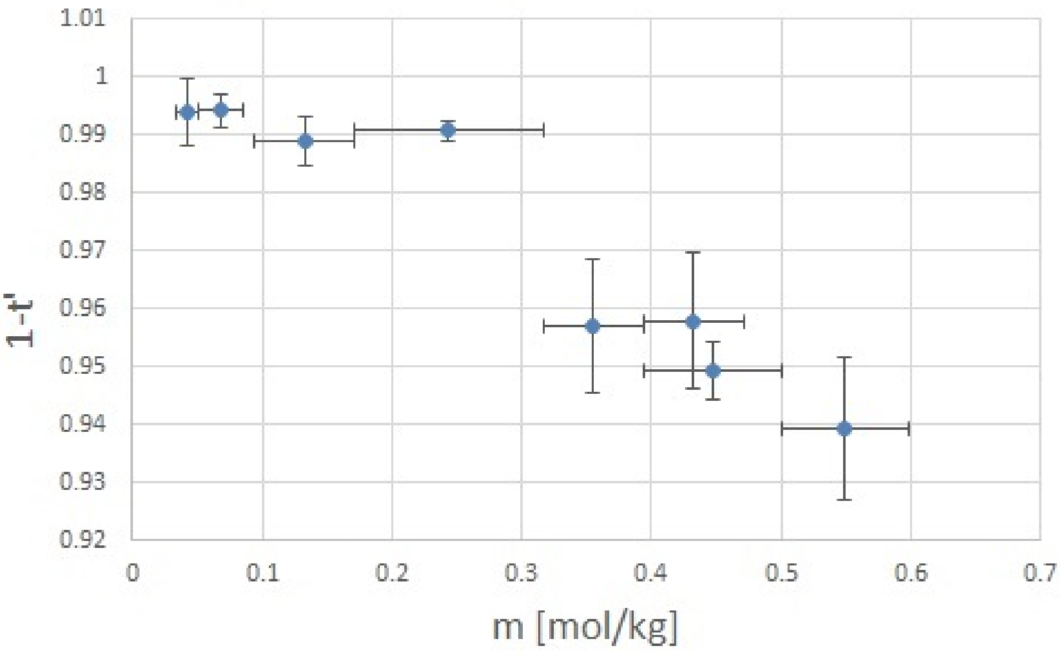

Figure 11: The apparent transport number of Cl^- as a function of the concentration of NaCl

The point is placed at the average of the concentrations used in the group of experiments. The horizontal error bars represent the concentration range t' is assumed to be constant. The vertical error bars show two standard deviations of the uncertainty in t' caused by the uncertainty in E. The uncertainty caused by the assumption is not accounted for. For both Figure 10 and Figure 11 the t' is calculated from an average of the measured E. The results from the following figure follows the same procedure as the results illustrated in figure 11, but instead of showing the average with error bars the calculated t' for each individual experiment is shown.

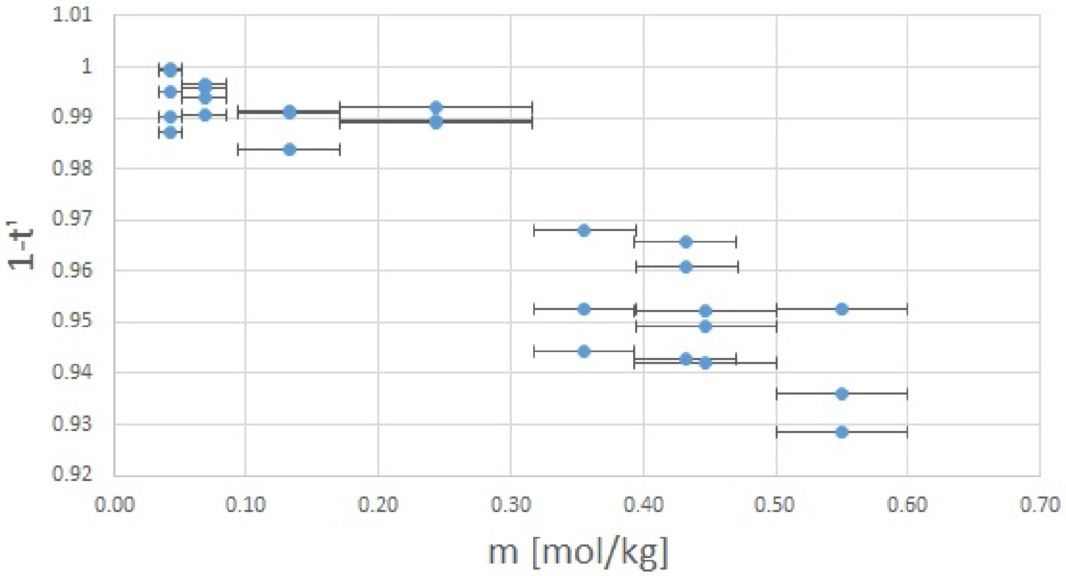

Figure 12: The apparent transport number for Cl^- as a function of the concentration of NaCl.

Figure 10 - 12 shows a downwards trend, meaning the membrane becomes less selective at higher concentrations. The concentration range t' is assumed to be constant in, is larger in figure 10, hence those results are less reliable. Of Figure 11 and 12, Figure 12 more clearly illustrate the results and the spread of the results. The results in Figure 12 will be used as a comparison to the results given by multiple linear regression.

3.4.3 Results from regression

To calculate the coefficients in Equation 17 the number of terms to include must be decided first. Therefore t'(m) was first found with only one term, then the number of terms were increased. The result for just one term (constant t') is shown in the Figure 13.

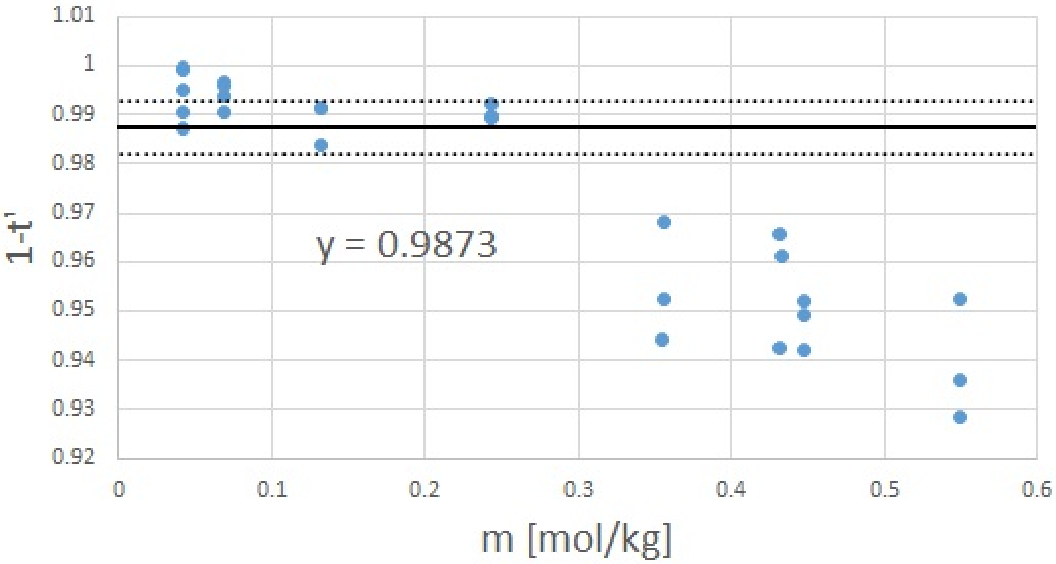

Figure 13: The apparent transport number of Cl^- as a function of salt concentration. The line shows the result from regression and the equation describe this line. The dotted lines show two standard deviations of the solid line. The dots show the results for Figure 12.

The trend line from regression does not match the results from Figure 12. While the results shown in Figure 12, shown here as dots, is not exactly right because of the assumption of a constant t' over a concentration range, they should be approximately right. Keep in mind the trend line from regression is not based on the results shown in Figure 12, but calculated directly from the data in Table 3. One term does not seem to be enough. In Figure 14 two terms have been included.

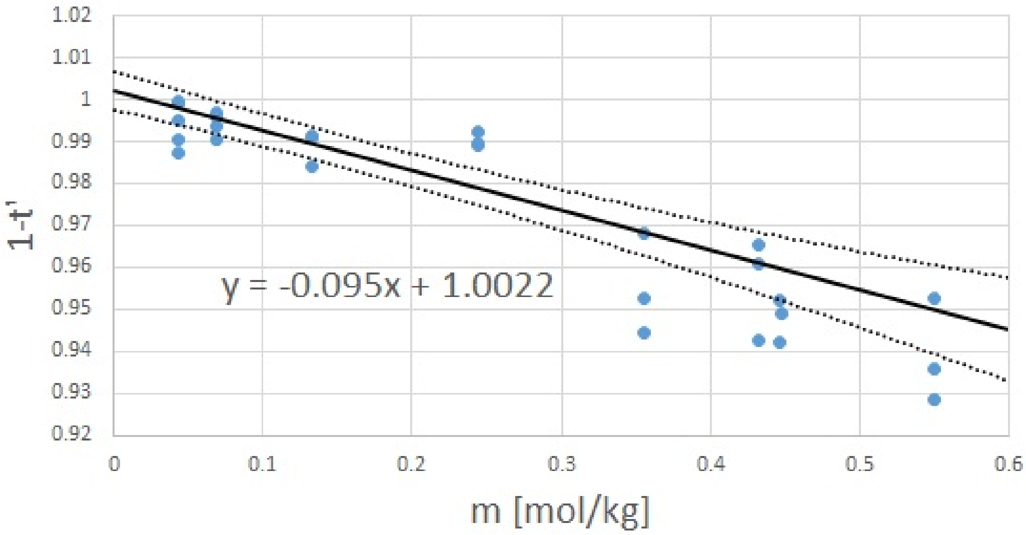

Figure 14: The apparent transport number of Cl^- as a function of salt concentration. The line shows the result from regression and the equation describe this line. The dotted lines show two standard deviations of the solid line. The dots show the results for Figure 12.

Here a linear trend is assumed. According to the equation shown in the figure, 1-t' is above 1 at zero concentration. This is not possible as the transport number must be between 0 and 1, and it would be negative if this were true. This point to the fact that the constant term of t' is either zero or close to zero. In Figure 15 a linear trend is still assumed, but the constant term is set to zero.

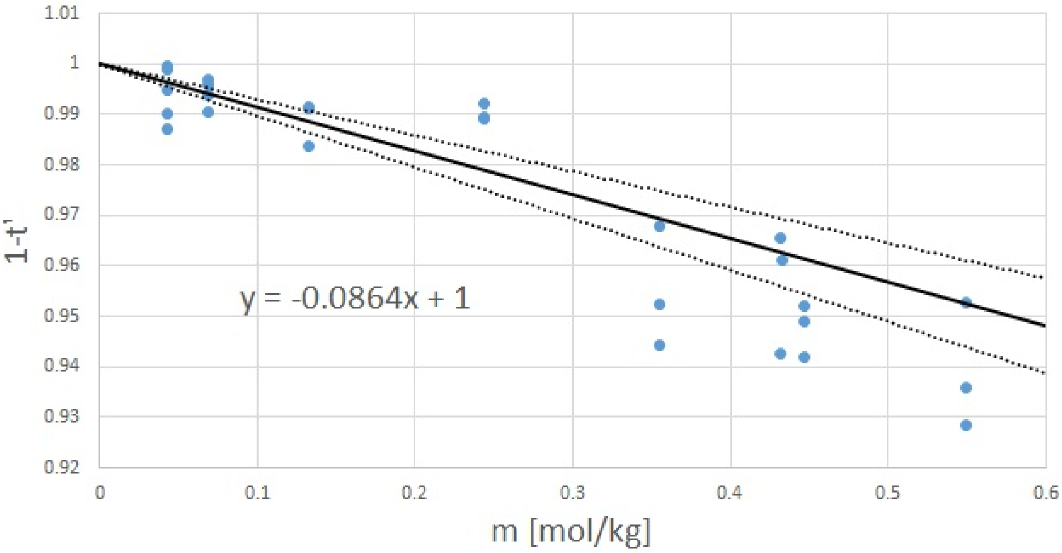

Figure 15: The apparent transport number of Cl^- as a function of salt concentration. The line shows the result from regression and the equation describe this line. The dotted lines show two standard deviations of the solid line. The dots show the results for Figure 12.

The trend line from regression matches the results from Figure 12. It does not match them perfectly, but this is to be expected, since those results are based on the assumption that t' is constant over a concentration range, while the trend line from the regression is not.

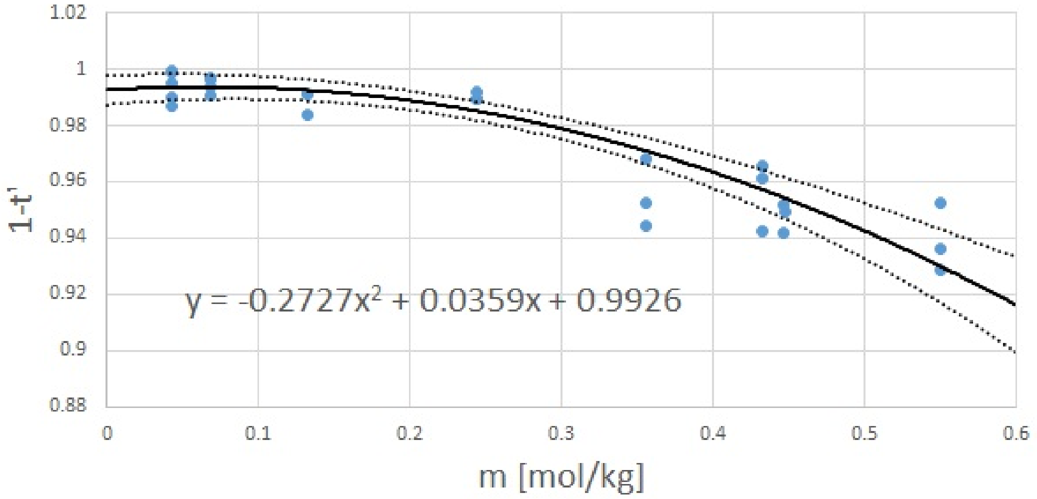

Figure 16: The apparent transport number of Cl^- as a function of salt concentration. The line shows the result from regression and the equation describe this line. The dotted lines show two standard deviations of the solid line. The dots show the results for Figure 12.

Here t' is modeled as a second order polynomial of m. The figure shows a maximum. This is not in agreement with Equation 29. A third order polynomial is shown in Figure 17.

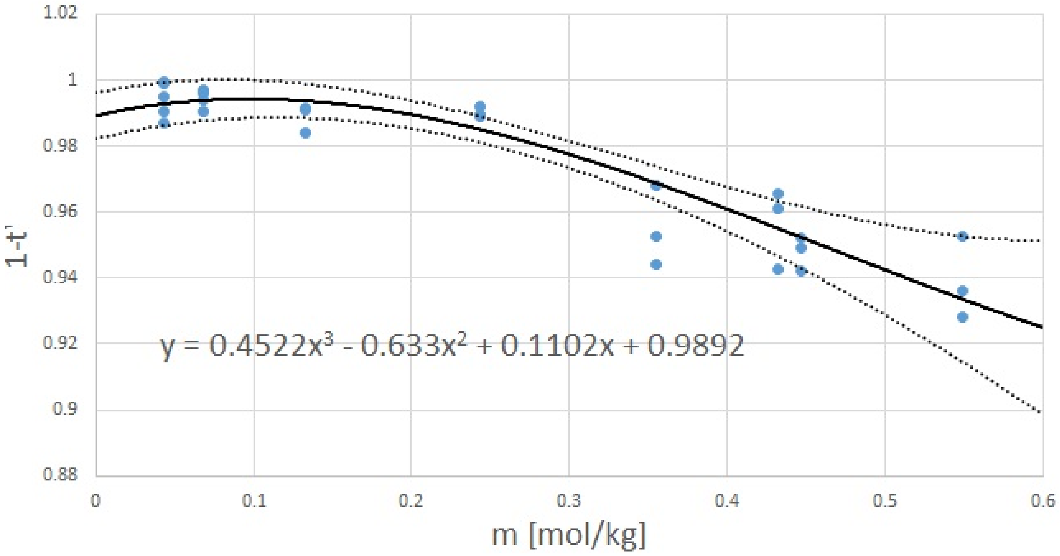

Figure 17: The apparent transport number of Cl^- as a function of salt concentration. The line shows the result from regression and the equation describe this line. The dotted lines show two standard deviations of the solid line. The dots show the results for Figure 12.

The higher order equation of t' seem to fit the results from figure 12 better, this could be partially because the higher order terms in Equation 44 is much smaller making the error caused by using Equation 13 smaller. Using higher orders run the risk of capturing the noise in the measurements in addition to the signal. This figure also shows a maximum.

If t_s and t_w is constant, then we would get an linear trend like in Figure 14 and 15. If we assume the trend is linear and t_s is zero, then t_w would be -4.8±0.8. That t_w is negative means it is transported by chloride ions, not sodium ions. This is to be expected, since almost 1 mol of chloride ions are transported through the membrane per mol electrons that are transferred between the electrodes, while almost no sodium are. Equation 17 can be written as:

$$t_w = -\frac{t'}{m * M_{H_2O}} + \frac{t_s}{m * M_{H_2O}} \tag{45}$$

Therefore if t_s is not zero, the absolute value of t_w would be smaller. A linear trend could also be caused by t_s increasing linearly with the concentration of salt, but if there is water transport in addition to this, one would expect positive second order term in t'(m).

The trend shown in Figure 12 can therefore be explained solely by the effect caused by the water transport/electroosmosis. The transport number of water would then by -4.8±0.8 This is in agreement with previous measurements where the average absolute water transport number of the anion and cation selective membranes used here was measured to be 11.7±2.1 [2], so it is reasonable to assume that this is the cause. To make anion membranes that perform better one should make therefore not make them more selective against cations, since it seems to be perfectly selective against them already, but instead make them selective against water. The transport number of water of different membranes have in the past been measured to 4-50 depending on the membrane [2, 3].

3.5 Results from cation selective membrane

Table 4 below shows the concentrations used in each experiment and the measured electric potential. The experiments are divided into groups where each group has the same concentration combination. There are twelve groups overall.

Table 4: Potential difference at different concentrations

m_1 [mol/kg]	m_2 [mol/kg]	E [V]
Group 1		
0.05	0.04	-6.9E-03
0.05	0.04	-7.4E-03
0.05	0.04	-7.2E-03
0.05	0.04	-7.3E-03
Group 2		
0.05	0.06	8.8E-03
0.05	0.06	8.3E-03
0.05	0.06	8.5E-03
0.05	0.06	8.7E-03
Group 3		
0.17	0.166	-1.4E-03
0.17	0.166	-1.4E-03
0.17	0.166	-1.4E-03
Group 4		
0.17	0.176	1.4E-03
0.17	0.176	1.4E-03
0.17	0.176	1.4E-03
Group 5		
0.30	0.26	-7.3E-03
0.30	0.26	-7.1E-03
0.30	0.26	-7.4E-03
0.30	0.26	-7.4E-03
Group 6		
0.30	0.36	8.3E-03
0.30	0.36	8.4E-03
0.30	0.36	7.8E-03
0.30	0.36	8.3E-03
Group 7		
0.39	0.38	-1.4E-03
0.39	0.38	-1.4E-03
0.39	0.38	-1.5E-03
Group 8		
0.39	0.41	1.3E-03
0.39	0.41	1.4E-03
0.39	0.41	1.4E-03
Group 9		
0.50	0.45	-4.5E-03
0.50	0.45	-4.5E-03
0.50	0.45	-4.6E-03
Group 10		
0.50	0.48	-1.8E-03
0.50	0.48	-2.0E-03
0.50	0.48	-1.8E-03
Group 11		
0.50	0.51	7.8E-04
0.50	0.51	9.9E-04
0.50	0.51	9.6E-04
Group 12		
0.50	0.53	2.5E-03
0.50	0.53	2.1E-03
0.50	0.53	2.7E-03

The apparent transport number was calculated for each experiment using Equation 13. The results are shown in Figure 18.

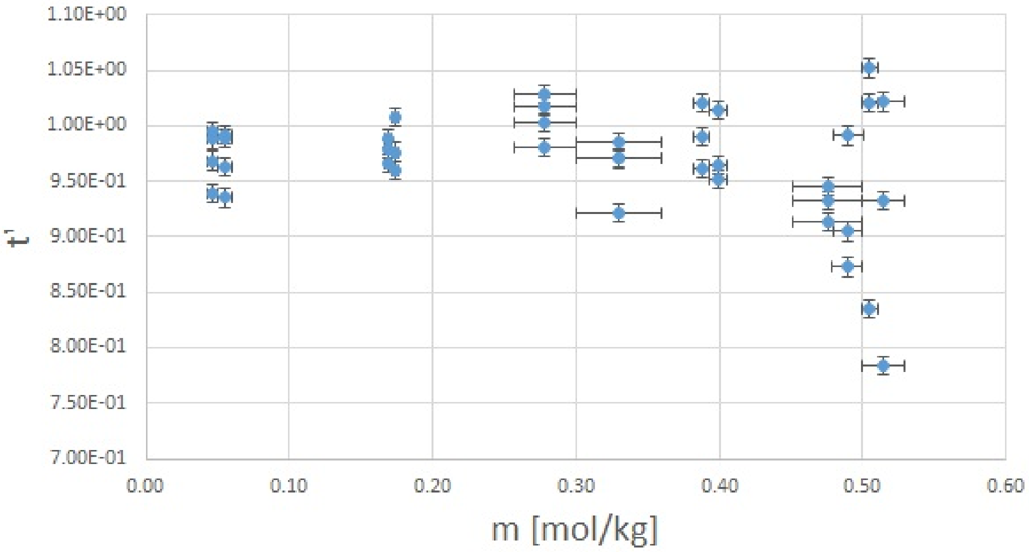

Figure 18: The apparent transport number measured for each experiment. The horizontal error bars indicate the concentration range used.

The results from Group 11 and 12 seem to be very uncertain since they are wider spread vertically than the rest of the groups. The results from Group 1 and 2 give apparent transport numbers a little above 1 which is not possible. This is caused by the uncertainty in the measurements. Figure 19 shows the apparent transport number as a function of concentration found with multiple linear regression, if the results from Group 11 and 12 are excluded. The apparent transport number has been assumed to vary linearly with the concentration.

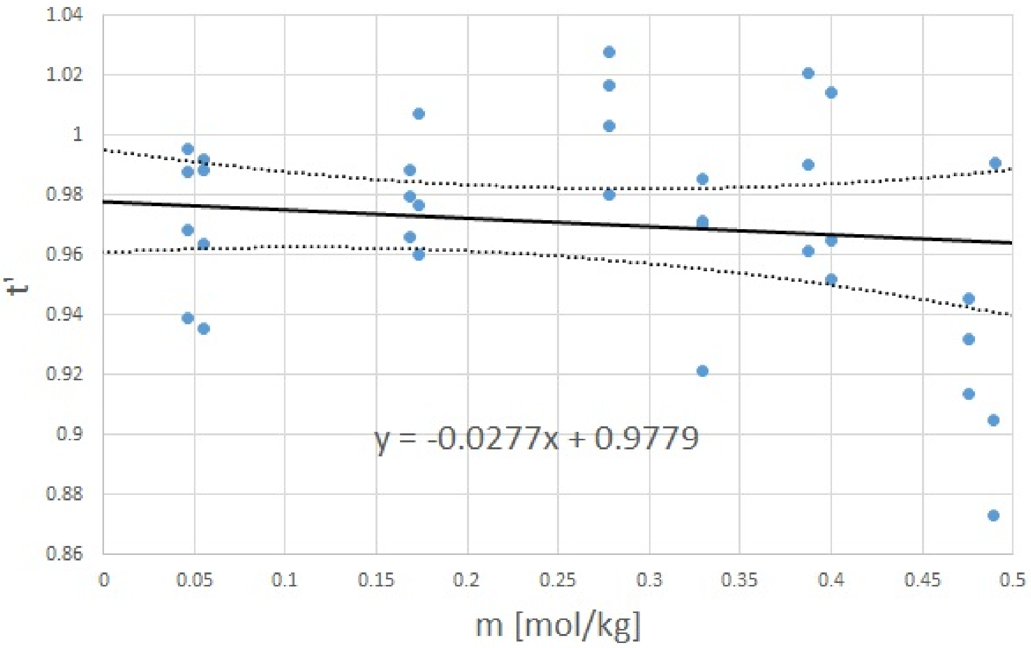

Figure 19: How the apparent transport number vary with concentration.

The dots are the results from individual experiments like in Figure 18. The line is from multiple linear regression of the data from every experiment except Group 11 and 12. The line is shown with two standard deviations. Assuming the trend is caused by electroosmosis we get a water transport number of 2±4 and a salt transport number of 0.98±0.02. If the salt transport number is assumed to be 1, then the water transport number would be 5±1.

The trend line does not fit the results from Figure 18 very well. In Figure 20 below, t'(m) is assumed to be a second order polynomial.

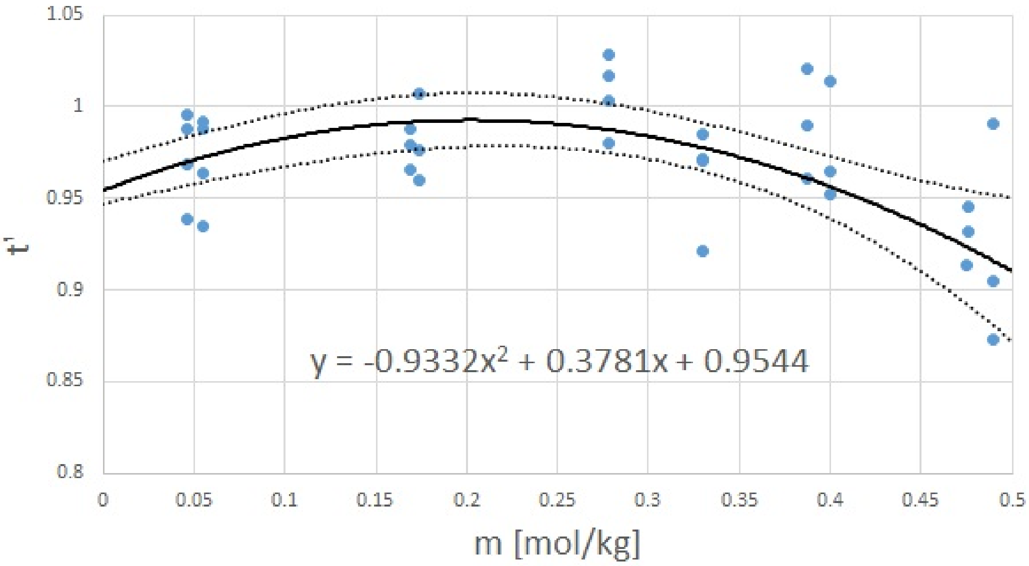

Figure 20: How the apparent transport number vary with concentration.

In Figure 20, t'(m) is modeled as second order polynomial. The second order coefficient is negative and the first order coefficient is positive. This goes against the predictions made in Section 2.4.

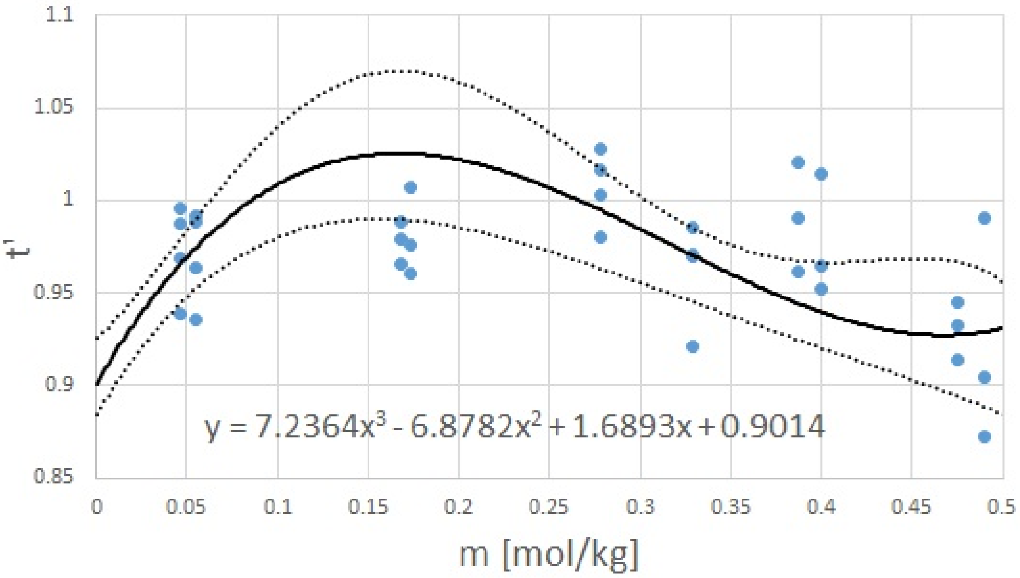

Figure 21: How the apparent transport number vary with concentration.

In Figure 21, t'(m) is modeled as a third order polynomial. As in Figure 20 t'(m) has a maximum and the signs of the coefficients do not match those predicted in Section 2.4. The experiments with the cation selective membrane were done before the experiments with the anion selective membrane so it is likely more mistakes have been made with these measurements. The concentration difference used was smaller than with the anion selective membrane. This means the measurements would be more sensitive to changes in the concentration caused by leaks, evaporation and diffusion. However, the amount of diffusion is less when the concentration difference is smaller. Uncertainties in the concentration caused by small errors when making it would also be more significant. From Figures 18-21 it looks like the apparent transport number does not decrease except at the end. This could be interpreted as the cation selective membrane not having much water transport, meaning the transport number of water would be close to zero. This is likely not the case since the water transport number of the anion selective membrane was estimated to be -4.8±0.8 and the average of the absolute water transport numbers have previously been measured to be 11.7±2.1 [2].

3.5.1 Concentration difference over a cation selective membrane

Equation 16 predicts that the apparent transport number will be larger at larger concentration differences if the highest concentration is kept constant. The measured electric potential at different concentration differences is shown in Table 5.

Table 5: The concentrations used and the measured potential

m_1 [mol/kg]	m_2 [mol/kg]	E [V]
Group 1		
0.50	0.48	-1.8E-03
0.50	0.48	-2.0E-03
0.50	0.48	-1.8E-03
Group 2		
0.50	0.45	-4.5E-03
0.50	0.45	-4.5E-03
0.50	0.45	-4.6E-03
Group 3		
0.5	0.36	-1.4E-02
0.5	0.36	-1.4E-02
0.5	0.36	-1.5E-02
Group 4		
0.5	0.26	-3.0E-02
0.5	0.26	-3.0E-02
0.5	0.26	-3.1E-02
0.5	0.26	-3.1E-02
0.5	0.26	-3.0E-02
0.5	0.26	-3.1E-02
0.5	0.26	-3.1E-02
0.5	0.26	-3.0E-02

The apparent transport number calculated from the data in table 5 is shown in Figure 22.

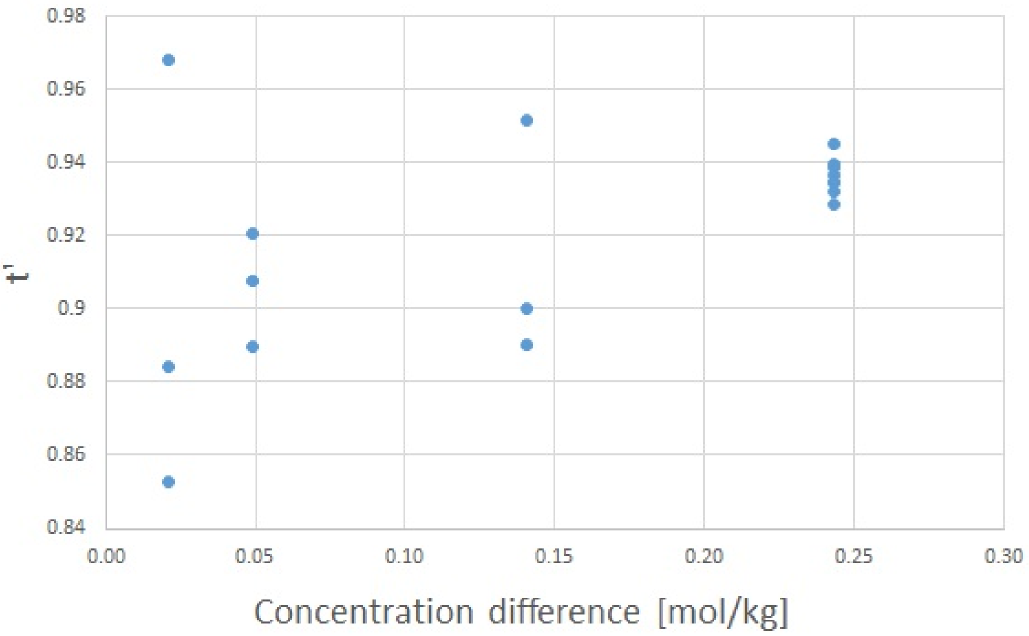

Figure 22: The measured apparent transport number as a function of concentration difference.

The uncertainty is greater at lower concentration differences, since the potential is lower and therefore the uncertainty in the measurements are comparatively larger. The apparent transport number seems to increase with increasing concentration difference, but there is a lot of uncertainty, so it is hard to tell. If the transport number of sodium is assumed to be 1, the water transport number calculated from the data in Table 5 will be 4±1.

3.6 Summary of experimental results

The anion selective membrane Fumasep FAD behaves as if it is perfectly selective and has a water transport number of -4.8±0.8. The cation selective membrane does not behave as predicted in Section 2. This is likely caused by experimental error. The results are discussed in more detail in Section 5.2.

4 Simulation

In Section 2 it is proposed that non-ideal apparent transport numbers could be caused by electroosmosis. This is supported by the experimental results in Section 3. This is in opposition to the common interpretation that the apparent transport number is a measurement of the membranes selectivity and treated like a constant. This interpretation, that non-ideal apparent transport numbers is caused by electroosmosis, has implications on simulation of RED stacks. In this section, the impact of the different interpretations of the apparent transport number on the total salt flux, total water flux and electric potential and power generation of a simple cell is investigated.

4.1 The system

The system that has been investigated is a model of a concentration cell with a cation selective membrane and electrodes reversible to chloride ions. Figure 23 below shows the modeled cell.

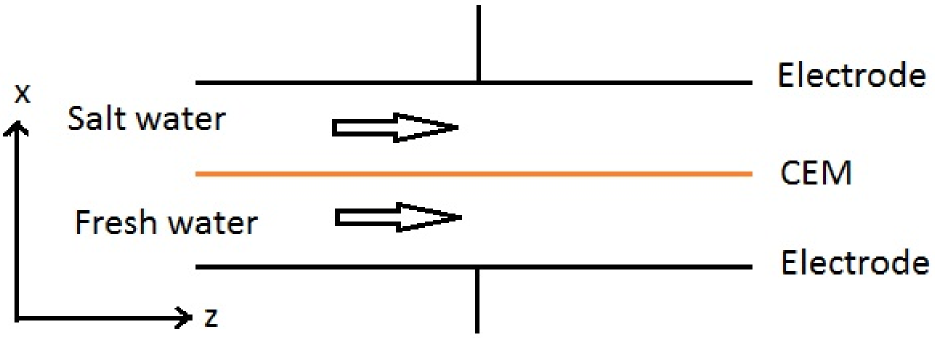

Figure 23: The arrangement of the system. CEM stands for cation exchange membrane, which is also called cation selective membrane.

A stream of ocean water and a stream of river water is separated by a cation selective membrane. Above and below these streams are plate electrodes of the same area as the membrane. This means the electrical potential between the two electrodes are the same everywhere in the system. The system described here is mathematically similar to a unit cell of a RED stack, which consists of a cation selective membrane and an anion selective membrane. With the assumptions made here (see Section 4.2) there is only a few differences. The water transport number would not be the water transport number of the cation selective membrane, but the sum of the absolute values of the water transport numbers for both the cation and anion selective membrane. The electrical resistance of the cation selective membrane would instead be the sum of the electrical resistances for the cation and anion selective membrane.

The selectivity of the selective membrane decides the performance of the concentration cell. The performance is related to the transference number as follows[22]:

$$\alpha_{CM} = 2t'^{CM}_{Na^+} - 1 \tag{46}$$

$$\alpha_{AM} = 1 - 2t'^{AM}_{Cl^-} \tag{47}$$

Where α is the selectivity, t'_{Na^+} is the apparent transport number for Na^+ and t'_{Cl^-} is the apparent transport number for Cl^-. The subscripts CM and AM signifies if the membrane is a cation or anion selective membrane. The sum of the apparent transport numbers for the ions are 1.

$$t'_{Na^+} + t'_{Cl^-} = 1 \tag{48}$$

If one measures the transport number by measuring the electric potential over a membrane and dividing it with the ideal potential, one would not get the true transport number if the transport number for water is non-zero.

$$E_{id} = -\frac{1}{F}\Delta\mu \tag{49}$$

Where E_{id} is the ideal electric potential for a perfectly selective membrane with no cotransport of water, F is Faradays constant and $\Delta\mu$ is the chemical potential between the two solutions.

$$t' = \frac{E}{E_{id}} = t_{Na^+} - t_w \frac{M_{H_2O}\int_{m_1}^{m_2} m\frac{d\mu}{dm}dm}{\Delta\mu} \tag{50}$$

Where t' is the apparent transport number, t_w is the transport number of water, t_{Na^+} is the transport number of Na^+, m is the molal concentration of NaCl, M_{H_2O} is the molar mass of water in kg per mol, m_1 and m_2 is the concentrations of NaCl in the two solutions.

In equation 50 it is assumed that the transport numbers do not change with the concentration. t' is a function of the concentrations of the solutions. The performance of a concentration cell has been modeled before [2], but it has been assumed that the measured t' is the same as t_{Na^+} and the electroosmosis caused by t_w not being zero was ignored. The effect of that assumption is what is investigated here.

4.2 Assumptions

The salt and fresh water has parallel flow with entry concentration of 3 and 30 g/l NaCl. Plug flow has been assumed, so the different solutions are mixed in all other directions than the flow direction. An exchange equilibrium between the membrane and the solution is assumed, which means a local equilibrium between the solution and the membrane at the solution-membrane interface. The flow rate (in kilograms of water per second) is assumed to be affected only by the water transport not the salt transport. The concentration in mol/l approximated as the concentration in mol/kg. The temperature is assumed to be constant everywhere in the system and possible temperature effects have been neglected. The obstruction caused by spacers has been neglected.

4.2.1 Flow regime

Whether the flow is laminar or turbulent is determined by the Reynolds number. The Reynolds number is calculated by this equation:

$$Re = \frac{vD_h}{\nu} \tag{51}$$

Where v is the mean velocity, ν is the kinematic viscosity and D_h is the hydraulic diameter. The hydraulic diameter for a rectangular duct is as follows:

$$D_h = \frac{2ab}{a+b} \tag{52}$$

Where a and b is the dimensions of the cross section of the duct.

For the flow rates used here the Reynolds number varies between 0.2 for low flow rates and 20 for high flow rates. The flow is laminar for Reynolds numbers below 2300, so the flow is laminar at these speeds and the solutions would not be mixed. This could cause concentration polarization and the concentration gradient over the membrane would be smaller than it if the solutions where mixed. The fluxes and the power extracted from the cell would therefore be smaller. Spacers could make the flow more turbulent.

4.3 Equations

The force-flux relations for the system are:

$$J_s = -L_{ss}\frac{d\mu_s}{dx} - L_{sw}\frac{d\mu_w}{dx} - L_{s\phi}\frac{d\Phi}{dx} \tag{53}$$

$$J_w = -L_{ws}\frac{d\mu_s}{dx} - L_{ww}\frac{d\mu_w}{dx} - L_{w\phi}\frac{d\Phi}{dx} \tag{54}$$

$$j = -L_{\phi s}\frac{d\mu_s}{dx} - L_{\phi w}\frac{d\mu_w}{dx} - L_{\phi\phi}\frac{d\Phi}{dx} \tag{55}$$

Where J_s is the salt flux, J_w is the water flux, j is the electric flux, L_{ij} is an Onsager coefficient, μ_s is the chemical potential of the salt, μ_w is the chemical potential of the water, Φ is the electric potential. The solutions are mixed within the saltwater and fresh water compartments. The equations describe the transport through the membrane.

The chemical potential of water at constant temperature and pressure can be eliminated by using the Gibbs-Duhem equation:

$$C_s d\mu_s + C_w d\mu_w = 0 \tag{56}$$

$$d\mu_w = -\frac{C_s}{C_w}d\mu_s = -mM_{H_2O}d\mu_s \tag{57}$$

Where C_s is the concentration of the salt in mol/l, C_w is the concentration of water in mol/l, m is molal concentration of NaCl and M_{H_2O} is the molar mass of water in kg per mol.

Substitute the chemical potential of water with Equation 57 and the force flux relations become:

$$J_s = -\left(L_{ss} - mM_{H_2O}L_{ws}\right)\frac{d\mu_s}{dx} - L_{s\phi}\frac{d\Phi}{dx} \tag{58}$$

$$J_w = -\left(L_{ws} - mM_{H_2O}L_{ww}\right)\frac{d\mu_s}{dx} - L_{w\phi}\frac{d\Phi}{dx} \tag{59}$$

$$j = -\left(L_{\phi s} - mM_{H_2O}L_{\phi w}\right)\frac{d\mu_s}{dx} - L_{\phi\phi}\frac{d\Phi}{dx} \tag{60}$$

Ficks law is assumed to be valid when there is no electric flux.

$$\left(J_i\right)_{j=0} = -D_i\frac{dC_i}{dx} \tag{61}$$

Where J_i and D_i is the flux and diffusion constant for component i, where i can be s for salt of w for water.

The transport numbers of sodium and water is defined as:

$$t_{Na^+} = F\left(\frac{J_{Na^+}}{j}\right) = F\left(\frac{J_s}{j}\right) = F\frac{L_{\phi s}}{L_{\phi\phi}} \tag{62}$$

$$t_w = F\left(\frac{J_w}{j}\right) = F\frac{L_{\phi w}}{L_{\phi\phi}} \tag{63}$$

Combining equations 61-63 with equation 58-60 we get:

$$J_s = -D_s \frac{dC_s}{dx} + t_{Na^+} j/F \tag{64}$$

$$J_w = -D_w \frac{dC_w}{dx} + t_w j/F \tag{65}$$

$$j = -\left(L_{\phi s} - mM_{H_2O} L_{\phi s}\right) \frac{d\mu_s}{dx} - L_{\phi\phi} \frac{d\Phi}{dx} \tag{66}$$

Where F is Faradays constant.

The concentration in mol/l can be substituted with the concentration in mol/kg by this relation:

$$\frac{dC_s}{dx} = \rho \frac{dm}{dx} \tag{67}$$

1 Where ρ is the density of water in kg/l.

We introduce the following assumption:

$$\frac{dC_w}{dx} \approx -\frac{dC_s}{dx} \tag{68}$$

The concentration difference of water is approximately the same as the concentration difference of salt [2]. This assumption was used in the determination of the diffusion coefficient used [2] and has previously been used in modeling of saline power cells [5].

With Equation 67 and 68 the force flux relations become:

$$J_s = -D_s \rho \frac{dm}{dx} + t_{Na^+} j/F \tag{69}$$

$$J_w = D_w \rho \frac{dm}{dx} + t_w j/F \tag{70}$$

$$j = -\left(L_{\phi s} - mM_{H_2O} L_{\phi s}\right) \frac{d\mu_s}{dx} - L_{\phi\phi} \frac{d\Phi}{dx} \tag{71}$$

Positive flux means that salt is transported from the ocean water compartment into the river water compartment.

The electrical resistance of the system is the sum of the resistances of the solutions and the membrane. The electrical resistance of one of the solutions is:

$$R = \frac{\Delta \mathcal{X}}{C_s \Lambda_m} \tag{72}$$

Where $\Delta \mathcal{X}$ is the width of the water compartment and Λ_m is the molar conductivity.

The molar conductivity is dependent on concentration. This dependency is described with the Debye-Huckel-Onsager equation:

$$\Lambda_m = \Lambda_m^0 - K\sqrt{C_s} \tag{73}$$

Where Λ_m^0 is the conductivity at infinite dilution and is a constant.

4.4 Mass balances

The mass balances for the salt is:

$$\frac{d(F_r m_r)}{dz} = F_r\frac{dm_r}{dz} + m_r\frac{dF_r}{dz} = J_s\Delta y \tag{74}$$

$$\frac{d(F_o m_o)}{dz} = F_o\frac{dm_o}{dz} + m_o\frac{dF_o}{dz} = -J_s\Delta y \tag{75}$$

$$\frac{dm_r}{dz} = \frac{J_s\Delta y}{F_r} - \frac{m_r}{F_r}\frac{dF_r}{dz} \tag{76}$$

$$\frac{dm_o}{dz} = \frac{-J_s\Delta y}{F_o} - \frac{m_o}{F_o}\frac{dF_o}{dz} \tag{77}$$

Where m is the molal concentration [mol/kg] of the salt. F is the flow rate of the water in kg/s. Subscript r stands for river water while subscript o stands for ocean water. Δy is the width of the membrane.

There is a water flux over the membrane which means the flow rate F also changes in the z-direction.

$$\frac{dF_r}{dz} = J_w\Delta y M_{H_2O} \tag{78}$$

$$\frac{dF_o}{dz} = -J_w\Delta y M_{H_2O} \tag{79}$$

Positive J_w means water get transferred from the ocean water to the river water. M_{H2O} is the molar mass of water in kg/mol.

Substitute dF/dz with Equation 78 and 79 and Equation 76 and 77 become:

$$\frac{dm_r}{dz} = \frac{J_s\Delta y}{F_r} - \frac{M_{H_2O} m_r J_w\Delta y}{F_r} \tag{80}$$

$$\frac{dm_o}{dz} = \frac{-J_s\Delta y}{F_o} + \frac{M_{H_2O} m_o J_w\Delta y}{F_o} \tag{81}$$

4.5 Matlab

Equations 69-71 and 78-81 was solved using ode15s. To compare the different interpretations of t' the simulations were run for $t_{Na^+} = 1$, $t_w = 10$ and for $t_{Na^+} = t'$, $t_w = 0$. t' was calculate with Equation 50 using the transport numbers for salt and water and the entry concentrations.

4.6 Input variables

Below is a table of the input variables in the model and their value.

Table 6: The input variables in the model

Variable	Value	Definition
Δx	0.1 mm	Thickness of the membrane
Δy	10 cm	Width of the membrane
$\Delta\mathcal{X}$	1 mm	Thickness of water compartments
Lz	10 cm	Length of the cell/membrane
Mr0	3 g/l NaCl	Entry concentration of the river water
Mo0	30 g/l NaCl	Entry concentration of the ocean water
Fr0	varies	Entry flow rate of the river water
Fo0	varies kg/s	Entry flow rate of the ocean water
E	varies	Electric potential between the electrodes
ts	1	Transport number of sodium in the membrane
tw	10	Transport number of water in the membrane
Ds	$1.3 * 10^{-11}$ (ms)$^{-1}$	Diffusion constant for the salt through the membrane [2]
Dw	$1.3 * 10^{-9}$ (ms)$^{-1}$	Diffusion constant for the water through the membrane [2]
Res	$5.90 * 10^{-4}$ Ω m^2	Electrical resistance of cation selective membrane [23]

In a real concentration cell, the potential between the electrodes can be controlled. The power output of the cell depends on this potential as shown in Figure 24 below.

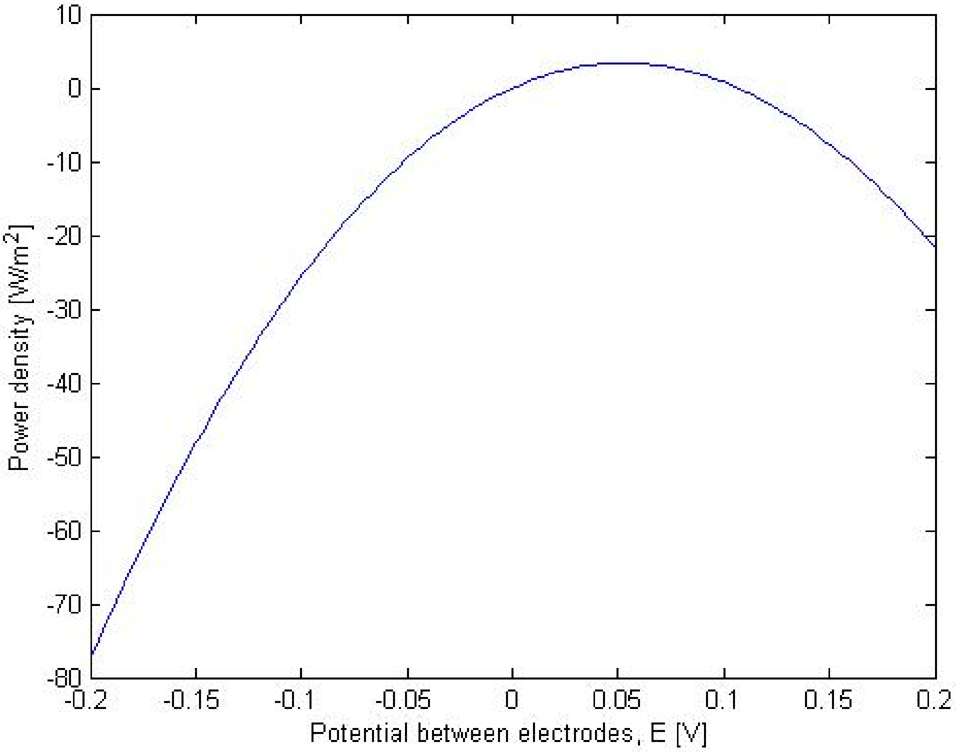

Figure 24: The power density of the cell as a function of the electric potential between the electrodes.

Here the flow rate is 1 cm/s and the other input variables are as stated in Table 6. The power output per area membrane goes through a maximum. In the simulations the potential E was chosen as that which gave the largest power output. The E value at the maximum power output will from now on be referred to as the electrical potential or the electrical potential between the electrodes. This was found with the Matlab function "fminbnd". The power output at this potential divided by the membrane area will be referred to as the maximum power density. The power density as a function of average electric flux is shown below.

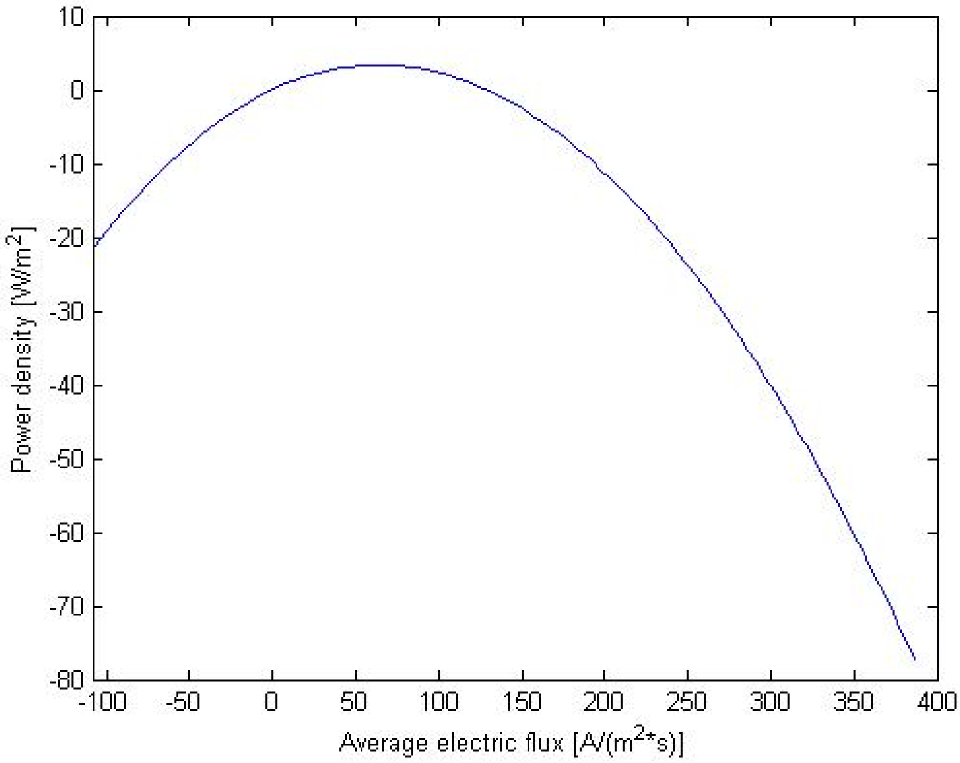

Figure 25: The power density as a function of the average electric flux of the cell.

The potential in Figure 24 determines the electric flux and the power density. Above is the relation between the average electric flux and the power density shown. The electric flux is different at different positions on the membrane the average electric flux is the total current divided by the membrane area.

4.7 Cases

If a membrane underperforms compared to an idealized membrane, that can be interpreted as the membrane not being perfectly selective or the membrane has electroosmotic transport of water. The goal of the simulations is to find out what difference these assumptions make on the maximum power output and electric potential. The apparent transport number used is the apparent transport number one would get if the transport number of sodium is 1 and the transport number of water is 10. The transport number of water has been measured to be around 4-50 in different commercial membranes [2, 3]. If the non-ideal apparent transport number was caused by water transport, it would depend on the salt concentrations used when it was measured. Therefore three different cases where simulated as described in below.

Case 1: The transport number of sodium is 1 and transport number of water is 10.

Case 2: The transport number of sodium is the apparent transport number and does not change with concentration. The apparent transport number is measured at the concentrations at the inlet: 3 g/l NaCl and 30 g/l NaCl. The transport number of water is 0.

Case 3: The transport number of sodium is the apparent transport number and does not change with concentration. The apparent transport number is measured at concentration different from the concentrations at the inlet: 20 g/l NaCl and 30 g/l NaCl. The transport number of water is 0.

The results from Case 1 was compared to the results from Case 2 and 3.

4.8 Results

Table 7 shows the calculated fluxes using the two interpretations. The flow rate was set to 1 cm/s.

Table 7: Size of water and salt flux in the different cases.

	Total water flux [mol/s]	Total salt flux [mol/s]
Case 1	1.2E-06	1.2E-07
Case 2	-1.1E-10	1.1E-07
Case 3	-2.0E-10	5.9E-06

If the unideal behavior of the membrane is caused by electroosmosis like in Case 1, then the water flux would be much larger (approximately equal to the salt flux times the water transport number) and in the opposite direction. The salt flux would also be larger. For Case 3 a smaller concentration difference was used when the apparent transport number was calculated, so the apparent transport number is smaller. Interpreting it as the transport number of sodium leads to a smaller predicted salt transport. The water flux is larger in Case 3 than in Case 2 since the concentration would change less along the cell and the concentration difference is what drives the water diffusion, which is the only cause of water flux in Case 2 and 3. The including electroosmosis gives a water flux of the opposite sign, so including the diffusion of water without electroosmosis makes the model less valid not more.

The optimum potential at which the power output is greatest is compared for Case 1 and 2 in Figure 26. The water transport number is here 10.

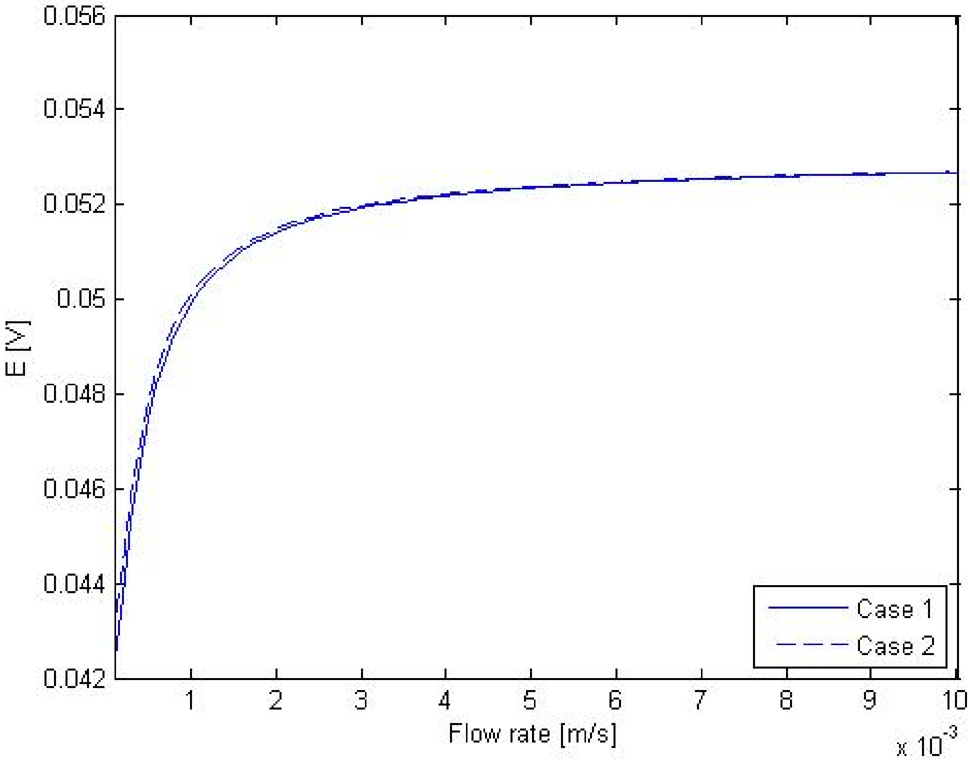

Figure 26: The electric potential between the electrodes at maximum power density as a function of the flow rate.

The flow rate kept the same for the fresh water and the saltwater. From the figure it does not look like there is much of a difference. The difference in fluxes have larger effect for lower flow rates where this would result in different concentrations, although it is still quite small. The difference between the potential from Case 2 and Case 1 in Figure 26 as a function of the flow rate is shown in Figure 27.

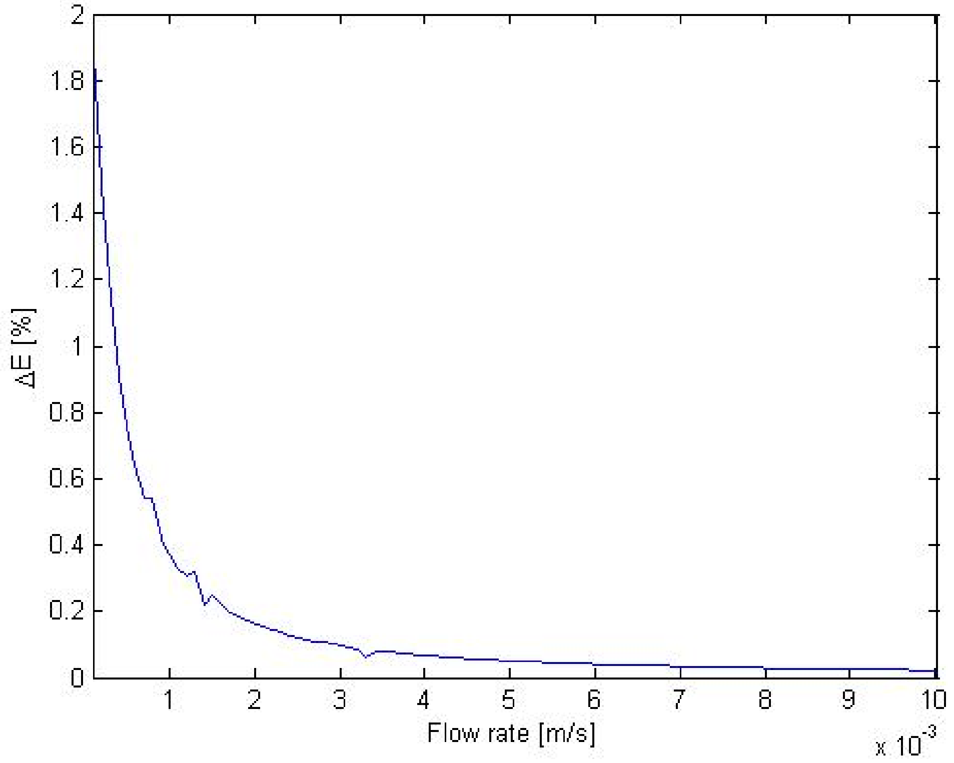

Figure 27: The difference between the two potentials as a function of the flow rate.

This is the percentage difference between the potential from Case 2 and Case 1 in Figure 26. Due to numerical inaccuracies it is not completely smooth. Below is the maximum power output as a function of flow rate. The lowest flow rate is 0.1 mm/s. The difference seems to increase when the flow rate decrease. This is because the fluxes over the membrane become larger compared to the amount of solution entering at the inlet when the flow rate decreases. Accurately calculating the fluxes through the membrane therefore matters more at lower concentrations.

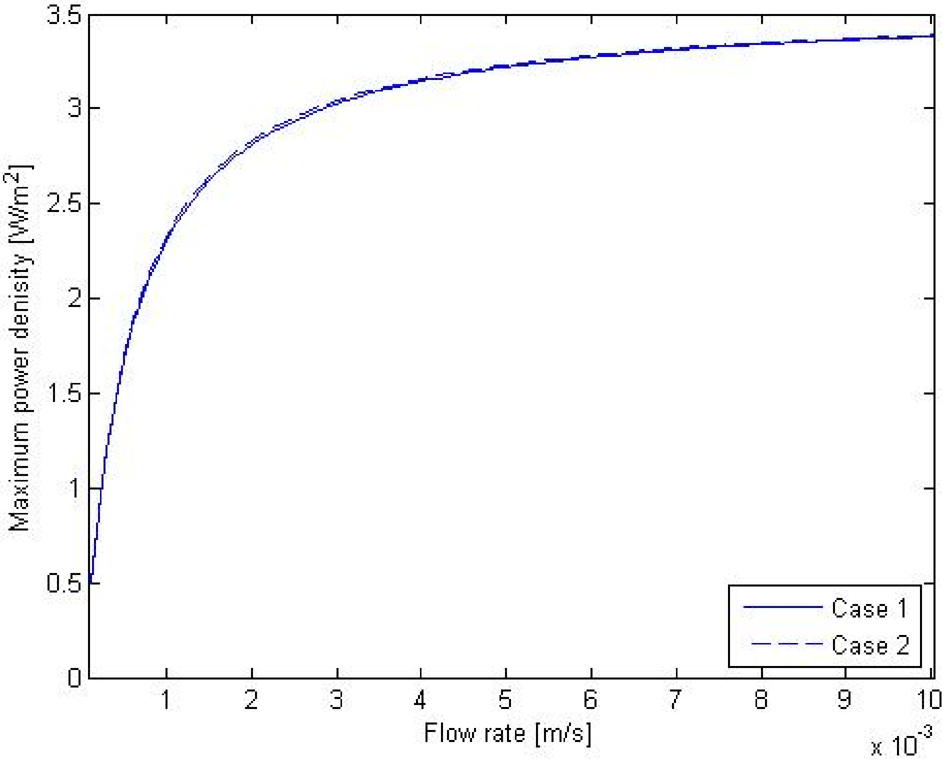

Figure 28: Maximum power density as a function of flow rate.

There is not much difference here either and the differences disappear at higher flow rates. This is because the transferred salt and water becomes negligible compared to the feed, and the concentrations become almost constant along the membrane. Case 1 and 2 have the same apparent transport number at the inlet concentrations. If the concentrations along membrane are always the same as at the inlet, the electric potential would be the same in either case. The power density depends on the potential, so it would be the same too.

In Figure 29 is the optimum potential at which the power output is greatest compared for Case 1 and 3.

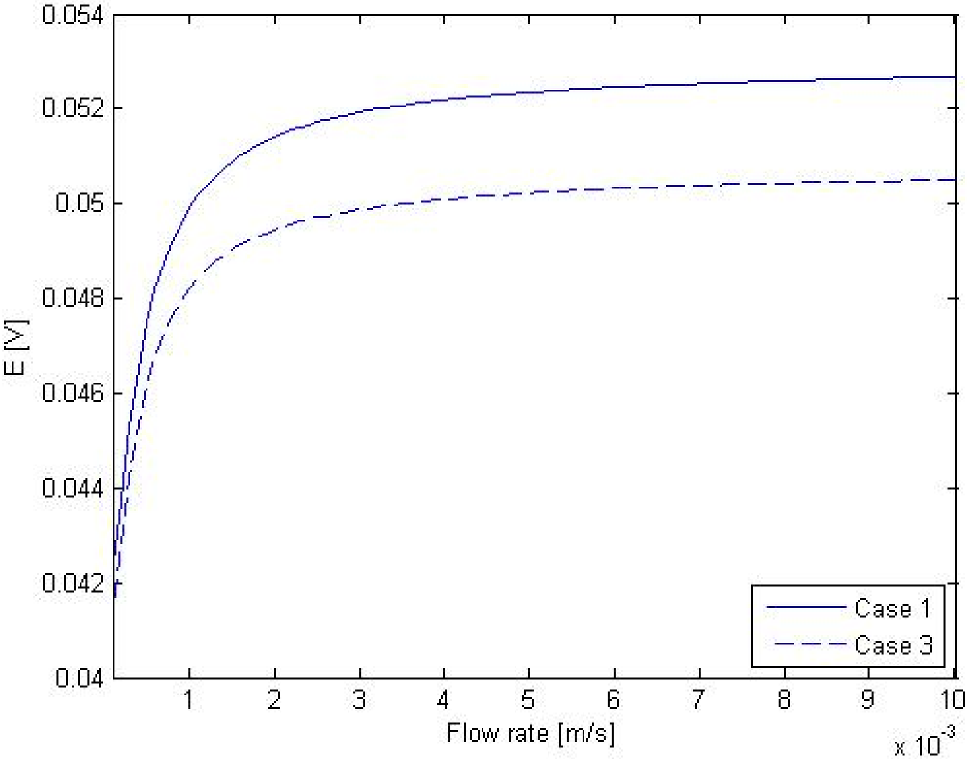

Figure 29: The electric potential between the electrodes at maximum power density as a function of the flow rate.

The difference here is larger than between Case 1 and 2 and the two functions no longer converge at high flow rates. The difference in the potential from Case 3 and Case 1 is shown in Figure 30.

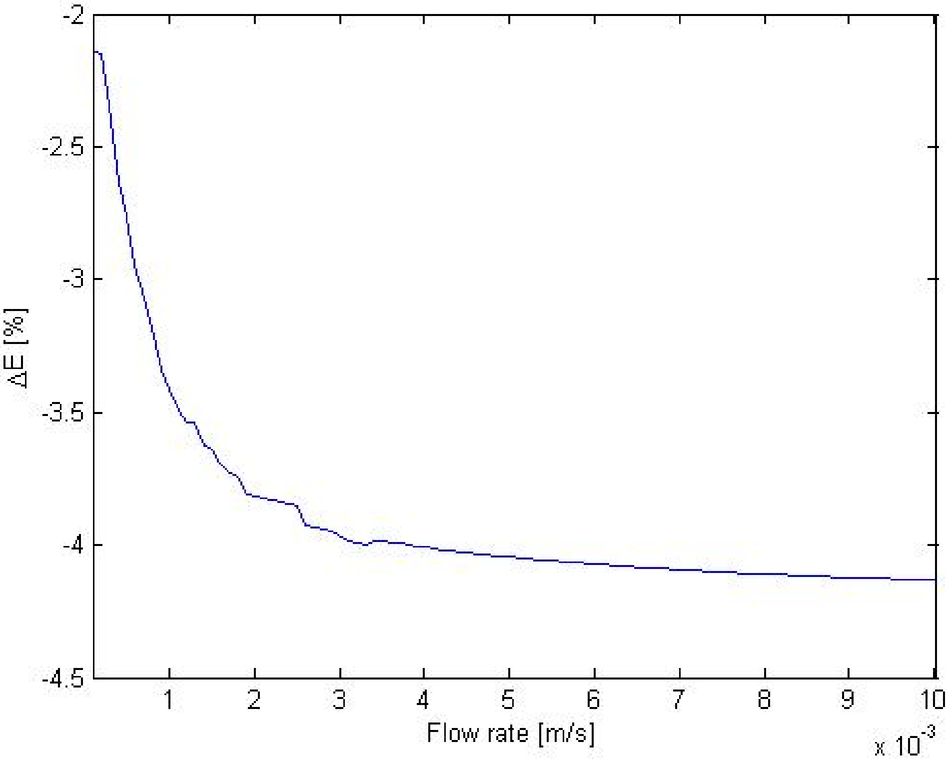

Figure 30: The difference between the two potentials as a function of the flow rate.

This is the percentage difference between the potential from Case 3 and Case 1 in Figure 29. The difference seems to go towards 4-5% at high flow rates.

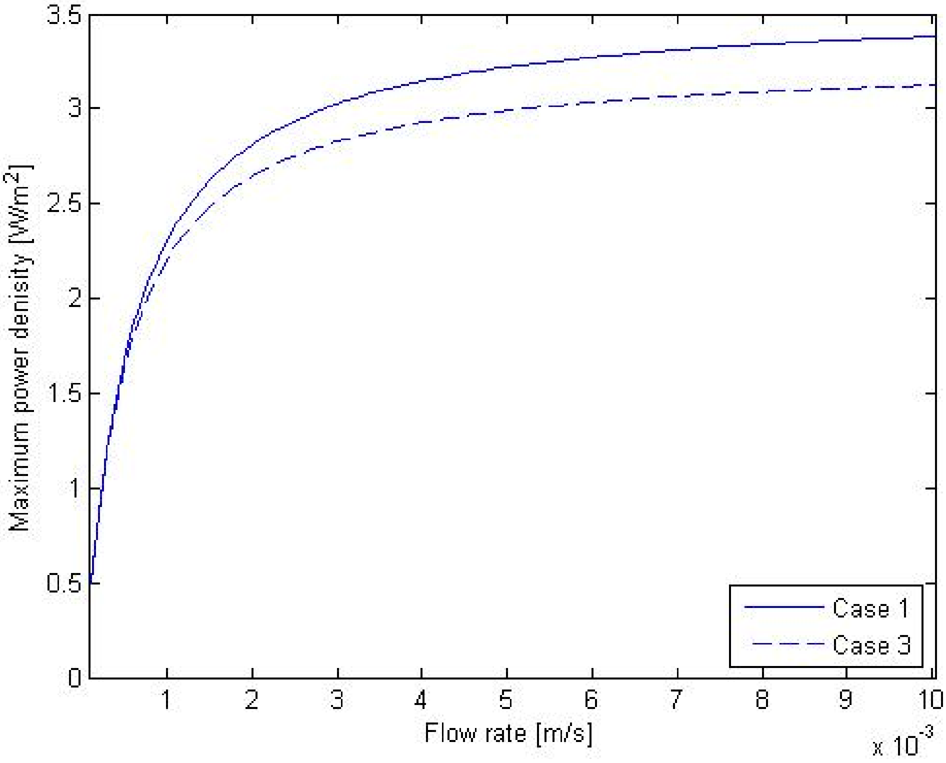

Figure 31: Maximum power density as a function of flow rate.

The two functions go to different values as the flow rate increases. The difference is around 7 %.

5 Discussion

In Section 5.1 the expression commonly used to calculate the measurable electric potential over a membrane (Section 5.1.1) as well as a boron nitrate nanotube with an apparent transport number of 1.4 [1] (Section 5.1.2) is discussed. Subsequent sections are discussions about the experimental results (Section 5.2) and the results from simulations (Section 5.3).

5.1 Literature

5.1.1 Measurable potential

The equation for the measurable electric potential is derived from irreversible thermodynamics in Section 2.1.

$$E = -\frac{1}{F}\int_{m_1}^{m_2} \left(t_{Na^+} - mM_{H_2O}t_w\right)\frac{d\mu_s}{dm}dm \tag{82}$$

Even if there is no transport of water and the transport number of water is zero, this expression is very different from what is commonly used. The following equation is often used to calculate the measurable potential over an ion selective membrane[22]. It is called the open circuit potential (OPC), Donnan potential or liquid junction potential.

$$E_{OCP} = -\frac{1}{2F}(t_{Na^+} - t_{Cl^-})\Delta\mu_s = -\frac{1}{2F}(2t_{Na^+} - 1)\Delta\mu_s \tag{83}$$

Where E_{OPC} is open circuit potential. The logic behind this equation is that it has two contributions: one from the sodium ion and one from the chloride ion. One considers the chemical potential of the sodium ion μ_{Na^+} and the chemical potential of the chloride ion μ_{Cl^-}. The ions travel in opposite directions so one must go against it's chemical potential and it's contribution is therefore of the opposite sign. For each mol electrons that travels between the electrodes t_{Na^+} mol sodium is transferred through the membrane and t_{Cl^-} mol chloride ions travel in the opposite direction. Equation 84 can then be derived using the Nernst equation.

$$E_{OCP} = -\frac{1}{F}(t_{Na^+}\Delta\mu_{Na^+} - t_{Cl^-}\Delta\mu_{Cl^-}) \tag{84}$$

This becomes Equation 83 if one assume:

$$\Delta\mu_{Na^+} = \Delta\mu_{Cl^-} = \frac{1}{2}\Delta\mu_s \tag{85}$$

Equation 83 will not give the measurable electric potential even when there is no water flux, since when the potential is measured by electrodes and the electrode reactions are ignored. Sodium ions can not be transferred into a solution with the cotransport of chloride ions because the system has to obey the law of electronutrality. This is not taken into account in the derivation of Equation 83. If electrodes reversible to the anion is used 1 mol of chloride ions will get absorbed on one electrode and 1 mol will get released on from the other. Let us say we have Solution 1 and 2 on each side of the membrane. In Solution 1 a mol of chloride ions will be absorbed by the electrode, t_{Na^+}

mol sodium ions is transferred to Solution 2 and t_{Cl^-} mol chloride ions is transferred into Solution 1 from Solution 2. The $t_{Cl^-} = 1 - t_{Na^+}$ the overall transfer is t_{Na^+} mol NaCl from Solution 1 to Solution 2. The correct equation for the measurable electric potential when there is no water transport would then be:

$$E = -\frac{1}{F} t_{Na^+} \Delta\mu_s \tag{86}$$

Hence the potential over a cation selective membrane will be equal to the ideal potential, if it is perfectly selective and there is no water transport. The potential over a perfectly selective anion selective membrane with no water transport will be zero. If the transport number is 0.5 the potential will be half the ideal potential. This is very different from what one gets from Equation 83 where the potential is zero if the transport numbers are 0.5.

The expressions for permselectivity (apparent transport number) of ion selective membranes from Equation 83 are:

$$\alpha_{CM} = 2t_{Na^+} - 1 \tag{87}$$

$$\alpha_{AM} = 2t_{Cl^-} - 1 \tag{88}$$

Where α_{CM} is the permselectivity of the cation selective membrane and α_{AM} is the permselectivtity of the anion selective membrane. These are not correct and if the transport numbers are calculated from these equations one would get the wrong results. The equation for the unit cell potential, the repeating unit in a RED stack, based on Equation 83, 87 and 88 is:

$$E_{unit} = -\frac{1}{2F}(\alpha_{CM} + \alpha_{AM})\Delta\mu_s \tag{89}$$

Where E_{unit} is the unit cell potential. While Equation 83, 87 and 88 are wrong, this will give the same answer that one would get from using Equation 86. It can also be written as:

$$E_{unit} = -\frac{1}{F}(t^{CM}_{Na^+} - t^{AM}_{Na^+})\Delta\mu_s \tag{90}$$

Equation 89 is not correct if there is water transport through the membranes. Then the correct expression would be:

$$E_{unit} = -\frac{1}{F}\int_{m_1}^{m_2} \left(t^{CM}_{Na^+} - t^{AM}_{Na^+} - mM_{H_2O}(t^{CM}_{w} - t^{AM}_{w})\right)\frac{d\mu_s}{dm}dm \tag{91}$$

5.1.2 Apparent transport numbers greater than 1

In Section 2.5 it was shown that apparent transport numbers above 1 is theoretically possible. At the time apparent transport numbers above 1 have not been reported, but a transport number of 1.4 can be calculated from the results shown in Figure 13 in the supplementary information of a recent Nature article (see Ref. [1]). Here the selective membrane consists of an impermeable part with a single boron nitride nanotube embedded in it. The nanotube connects the two solutions of KCl. The sides of the tube is negatively charged so it is selective for cations, but the Debye lengths do not overlap so it is not perfectly selective.

What could be the case is that the sodium travels along the sides of the nanotube since they are charged, while the chloride moves in the opposite direction in the middle of the tube. The tube is completely filled with water and since the more water in the membrane the more is transported by the pumping of the ion, this could cause the water flow to go from the diluted solution into the concentrated. Hence the salt is transferred from the concentrated to the diluted and the water from the diluted to the concentrated. Less salt is transferred than if the membrane was perfectly selective, but if the water transport is high enough it could more than make up for it. The absolute value of Gibbs energy of the reaction would then be greater than if only salt was transported. One can see from Figure 3 in Ref. [1] that the sign of the streaming current support this interpretation. Figure 3 in Ref. [1] is the result from a different experiment than the one used to calculate the apparent transport number, which had no pressure difference between the two solutions. The high pressure is at the positive electrode and the current goes from the positive electrode to the negative, meaning the electrons goes from the negative electrode to the positive. The water transport which goes from high pressure to low, from the positive electrode to the negative, therefore must carry with it negative ions. The overall transfer of water is therefore coupled with the transfer of chloride ions. Hence when there is a concentration difference, the water will be transported in the same direction as chloride ions from the diluted to the concentrated.

Assuming the water transport of sodium is negligible, the water transported per ion can be calculated using Equation 35 and 18. It also depend on the transport number of chloride. If it is assumed to be 0.2, then the number of water molecules transported per chloride ion would be 430. For higher transport numbers it would be less, like for 0.4 it would be 280. This was calculated using a third order polynomial model for the activity of KCl which was taken from Ref. [21]. The water transport number of water in polymer membranes are typically 4-50[2, 3]. The water transport number of the nanotube can be found with streaming potential measurements (see Ref. [17]). The large difference between the nanotube and the polymer membrane could be explained by the structural differences. The polymer membrane has a complicated structure of micro-channels [24] while the nanotube is a simple tube filled with water. As the hydrated ions move through the complicated network of channels it pushes the water ahead of it, but that water would not necessarily be pushed out the other side as it could be pushed into other channels. Thus in the polymer membrane the ions take different channels pushing and dragging the water in different directions in a network of narrow channels. While in the nanotube the ions enter on one side of a tube filled with water and exits on the other. A narrower channel would increase the friction of the water current and slow it down. The diameter of the nanotube in Ref. [1] was 60-80 nanometer. The pore size in polymer membranes vary, but a large portion have been measured to be under 0.2 nanometer in diameter in some membranes[25], so they are significantly smaller than the nanotube. The structure of the nanotube is therefore more conducive to create a water current from one side to the other. That the water transport is structure dependent has been reported before[26].

5.2 Experiments

The bias potential of the electrode subtracted from the measured Emf of the cell was found by taking the average between the measured bias potential in the solutions used. The bias potential during the measurements might not has been the average, so this is a source of uncertainty in the measurements. The bias potential is caused by differences in the electrode surface and change between each experiment. It might also have changed during the experiment. The uncertainty caused by the bias potential affect the measurements with the anion selective membrane more than with the cation selective membrane, since the measured potential is smaller and the bias therefore relatively larger. The results from the cation selective membrane where the concentration of both solutions were increased (see Figure 18) do not agree with the predicted trend in Section 2.1 or 2.4. The concentration difference used with the cation selective membrane was smaller than with the anion selective membrane. This means the measurements would be more sensitive to changes in the concentration caused by leaks, evaporation and diffusion. The amount of diffusion is less, when the concentration difference is smaller. Uncertainties in the concentration caused by small errors when making it would also be more significant. The experiments done with the cation selective membrane was the first experiments done, so they are more likely to be affected by human error due to lack of experience than the later experiments with the anion selective membrane. If the concentration dependency of the apparent transport number is assumed to be linear and caused by the water transport, one would get a water transport number of 2±4 and a salt transport number of 0.98±0.02. If the salt transport number is assumed to be 1, then the water transport number would be 5±1. The trend in Figure 18 is not linear. At first it appears to increase, and only decreases towards the end. One could interpret this to mean that the apparent transport number is constant before the concentration becomes large enough and the selectivity of the membrane diminishes. This would mean there is no or very little water transport through the cation selective membrane and the water transport number would be close to zero. This is likely not the case since water transport number of the anion selective membrane was estimated to be -4.8±0.8 and the average of the absolute water transport numbers have previously been measured to be 11.7±2.1 [2]. It is more likely that the measurements were not accurate enough, maybe because of human error.

There were also done measurements when one concentration were kept constant and the other lowered to increase the concentration difference. The theory predicts that the apparent transport number should go up with increased concentration difference under these circumstances. The experimental results seem to agree with this (see Figure 22), but there is a lot of uncertainty so it is hard to tell. If the transport number of sodium is assumed to be 1, the water transport number calculated from these data will be 4±1. Not much can be said about concentration dependency of the apparent transport number of the cation selective membrane based on the experiments performed here. More measurements are therefore needed.

The trend in the measurements from the anion selective membrane (see Figure 12) can be explained solely by the effect caused by the water transport/electroosmosis. The transport number of water would then be -4.8±0.8 if the membrane is perfectly selective, less than if it is not. The average absolute value of the transport number of water of the anion and cation selective membrane used is 11.7±2.1 [2], so it is reasonable to assume that this is the cause. The transport number of water of different membranes have in the past been measured to 4-50 depending on the membrane [2, 3]. The estimated water transport number of -4.8±0.8 can be controlled by finding the water transport number with streaming potential measurements (see Ref. [17]). It is not expected that the membrane will have this behavior at very large concentrations, since it will eventually lose selectivity, but if the membrane is going to be used for production of electricity only concentrations as high as the concentration of ocean water will be used. The concentration of ocean water is around 30 g/l NaCl.

Traditionally the apparent transport number has been interpreted as a measure of the selectivity of the membrane. The selectivity is caused by charged groups in the membrane polymer. Hence to make the membrane more selective, one might try to increase the amount of charged groups in the membrane. If the non-ideal behavior is caused by water transport, then this approach is not only non-effective, but counterproductive since the charged groups would make the membrane more hydrophilic [27, 28, 29, 30, 31, 32, 33]. A better approach would be to make the membrane more hydrophobic. The transport number of water can be determined with streaming potential measurements. The absolute value of which should be minimized if to make the membrane as efficient as possible.

5.3 Simulation

Including the electroosmotic contribution gives a higher flux of salt and water and the flux of water goes in the opposite direction. This means including diffusion of water without including the electroosmotic contribution would make the model less valid, not more. The reason the salt flux is higher is that the transport number of salt would be higher. The reason the water flux is higher is that the electroosmosis transfer far more water than diffusion does, and it is in the same opposite direction because the water is dragged along with the sodium ions against the water concentration difference. This affects the potential between the electrodes, but at flow rates above 1 mm/s it makes less than 1 % difference. It becomes more significant at low flow rates where the transferred water and salt is significantly large compared to the feed. At large flow rates using the apparent transport number as the transport number of sodium seem to be a good approximation when it comes to calculating electric potential and power output. However, this is only if the apparent transport number has been measured at the same concentration difference as the inlet. If it has been measured at other concentrations, this is not necessarily the case. For Case 3 which used 20 and 30 g/l NaCl instead of 3 and 30 g/l like in Case 2 the predicted power output was estimated to be about 7 % lower than in Case 1.

6 Conclusion

Manufactures are today able to make membranes with apparent transport numbers of around 0.9, values as high as 0.99 has been reported[7]. What has been shown here is that electroosmosis in most cases lowers the apparent transport number of ion selective membranes and make them concentration dependent where increasing the concentration of salt lowers the apparent transport number. With this understanding it is clear that this also should be controlled for. The degree and direction of electroosmosis can be described with the transport number of water in the membrane. The transport number of water should then in most cases be as close to zero as possible. It was also shown theoretically that electroosmosis could in some special cases give apparent transport numbers greater than 1. This is supported by the experimental results from a recent article.

The results from the experiments with the anion selective membrane gives the results one would expect from a perfectly ion selective membrane with a water transport number of -4.8±0.8 in the concentration range 2-30 g/l NaCl. This can be checked by finding the water transport number with streaming potential measurements. The way forward is then not to make membranes more selective against ions, but to make them selective against water.

The results from the cation selective membrane, where the concentration of both solutions on either side of the membrane was gradually increased, did not give the results one would expect from a membrane with water transport. Previous works have found that the average absolute water transport number of the cation and anion selective membrane used here is 11.7±2.1. The water transport is therefore not likely to be zero. The concentration dependency of the apparent transport number of sodium in the cation selective membrane shown in Figure 18 is therefore likely caused by some error in the measurement. There were also done experiments on the cation selective membrane with increasing concentration difference. These seem to agree with what is predicted in Section 2, but there is a lot of uncertainty so it is hard to tell. Further measurements on the cation selective membrane is therefore needed.

From the Matlab simulation it was shown that treating the apparent transport number as the transport number is good approximation, if the flow rate is high and the apparent transport number is measured at the concentration difference used in the RED cell. At lower concentration however the difference between interpreting the apparent transport number as the transport number and having it being caused by electroosmosis increases exponentially. If the apparent transport number is measured at different concentrations this approximation is inaccurate. If it is measured at the concentrations 20 and 30 g/l NaCl instead of 3 and 30 g/l NaCl the predicted electric potential would be 4-5 % lower and the predicted power output would be 7 % lower. This was with a water transport number of 10. A larger water transport number would give a larger difference. It is therefore important to measure the apparent transport number at the inlet concentrations if one wants to calculate the possible power output as it has been done previously. A better way is to use the water transport number and also include the electroosmosis in addition to the salt flux.

7 Suggested directions for further work

The anion selective membrane Fumasep FAD behaved as if it was perfectly selective with a water transport number of -4.8±0.8. Whether that is actually the case could be tested by streaming potential measurements, where the water transport number could be found. The validity of the equations in Section 2 could be tested further with experiments where one concentration remained the same and the other varied to increase the concentration difference like what was attempted here with the cation selective membrane.

The results from the cation selective membrane Fumasep FKD presented here were assumed to be caused by experimental error. The experiments with the cation selective membrane could be redone to see if it has the same behavior as the anion selective membrane. Using a higher concentration difference than the one that was used here is probably prudent (see Section 5.2). Doing streaming potential measurements on the cation selective membrane, would also give interesting results. If the cation selective membrane does not behave as the anion selective membrane, the results could help separate the effects of the electroosmosis and possible loss of selectivity.

These experiments could also be done on other membranes. Manufacturers are today able to make membranes with high apparent transport numbers. The membranes could already be perfectly selective. That their apparent transport numbers are less than 1, could be caused solely by the water transport. The results in Section 3 suggest that this is true for at least one membrane.

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