TITLE: Chloride reduction from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier

STUDENTS: Markus Hofmeister

Tobias Slusarek

Rafal Madaj

William Strömbäck

SUPERVISORS: Dr. Agustí Fortuny Sanromà, Universitat Politecnica de Catalunya

Dra. M. Teresa Coll Ausió, Universitat Politecnica de Catalunya

DATE: 03/06/2013
**TITLE:** Chloride reduction from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier

<table>
<thead>
<tr>
<th>FAMILY NAME:</th>
<th>Hofmeister</th>
<th>FIRST NAME:</th>
<th>Markus</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOME UNIVERSITY:</td>
<td>Technical University “Bergakademie” Freiberg, Germany</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPECIALITY:</td>
<td>Process Engineering</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FAMILY NAME:</th>
<th>Madaj</th>
<th>FIRST NAME:</th>
<th>Rafal</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOME UNIVERSITY:</td>
<td>Technical University of Lodz, Poland</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPECIALITY:</td>
<td>Biotechnology</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FAMILY NAME:</th>
<th>Slusarek</th>
<th>FIRST NAME:</th>
<th>Tobias</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOME UNIVERSITY:</td>
<td>University of Applied Sciences Kiel, Germany</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPECIALITY:</td>
<td>International Purchase and Sales Engineering</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FAMILY NAME:</th>
<th>Strömbäck</th>
<th>FIRST NAME:</th>
<th>William</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOME UNIVERSITY:</td>
<td>University of Applied Sciences Novia, Finland</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPECIALITY:</td>
<td>Industrial Engineering and Business</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Abstract

The project “Chloride reduction from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier” is about developing an alternative and cost effective solution for the Abrera drinking water treatment plant to desalinate water from Llobregat river while accomplishing drinking water standards. With a constant increase of the world’s population, the demand for drinking water also increases. However, the supply of drinking water is limited, so desalination as one part of water treatment is of essential need. The Llobregat river water, as one of the main sources of drinking water in the Barcelona metropolitan area, has a high content of dissolved salts wherefore even already treated water does not always fulfill the quality standards set by the European Union to be classified as “drinking water”. This is why the Abrera water treatment plant currently has to clean its water using the energy-intensive technique electrodialysis reversal.

Therefore an alternative technique, called Hollow Fiber Supported Liquid Membrane (HFSLM), has been investigated. This is a specialized application of new high-tech membrane technology supplying substance transport between two separated fractions using permeable membranes filled with ionic liquids. These liquids are characterized by a high concentration of available carrier molecules which enable these chemical systems to carry out mass transport particular selectively via ionic exchange between both the phases. Several experiments, using Aliquat® 336 as a representative phase transfer catalyst, have been conducted in order to obtain deepest understanding of the process taking place. As results, on one hand the functionality of this technique was proved and on the other hand delivered enough useful data to develop a scientific model of the transfer mechanism to predict its efficiency in a feasible up-scaled version for industrial use. Since the HFSLM technique as a concentration driven operation needs far less electricity than the common techniques electrodialysis reversal and reverse osmosis, it is already competitive in terms of running costs. The implementation costs on the other hand contain a big potential for improvement.

KEYWORDS Hollow Fiber, Supported Liquid Membrane, Chloride concentration reduction, Ionic liquid, Aliquat® 336, Phase transfer catalyst, Desalination, Abrera Drinking Water Treatment Plant
Table of contents

ABSTRACT .................................................................................................................................................... 3
TABLE OF CONTENTS .................................................................................................................................... 4
LIST OF FIGURES ........................................................................................................................................... 6
LIST OF TABLES ........................................................................................................................................... 9
1. INTRODUCTION ........................................................................................................................................ 10
2. WATER SHORTAGE ................................................................................................................................... 10
2.1. Freshwater ............................................................................................................................................ 10
2.2. What causes water shortage? ................................................................................................................ 10
2.3. Consequences of water shortage ........................................................................................................ 11
2.4. Basic approaches .................................................................................................................................. 11
3. CURRENT SITUATION IN THE BARCELONA REGION ........................................................................... 11
3.1. The current drinking water treatment procedure in Abrera .............................................................. 12
4. SALINITY .................................................................................................................................................. 13
4.1. Definition .............................................................................................................................................. 13
4.2. Common techniques of desalination ................................................................................................... 14
4.2.1. Electrodialysis .................................................................................................................................. 14
4.2.2. Reverse Osmosis .............................................................................................................................. 15
4.2.3. Purpose of membrane techniques ................................................................................................... 16
5. EXPERIMENTAL PART ............................................................................................................................ 17
5.1. General work principle ....................................................................................................................... 17
5.2. Investigation strategy .......................................................................................................................... 20
5.3. Phase transfer catalyst - Aliquat ® 336 .............................................................................................. 22
5.4. The bicarbonate anion ......................................................................................................................... 23
5.5. Equilibrium investigation and preparation of the phase transfer catalyst ........................................ 24
5.5.1. Background ...................................................................................................................................... 24
5.5.2. Procedure ....................................................................................................................................... 25
5.5.3. Results ............................................................................................................................................ 27
5.5.4. Conclusion ...................................................................................................................................... 34
5.6. Flat Sheet Supported Liquid Membrane (FSSLM) experiments ..................................................... 41
5.6.1. Background ...................................................................................................................................... 41
5.6.2. Procedure ....................................................................................................................................... 42
5.6.3. Results ............................................................................................................................................ 43
5.6.4. Conclusions ..................................................................................................................................... 45
5.7. Hollow fiber Supported Liquid Membrane (HFSLM) experiments ..................................................... 54
5.7.1. Background ...................................................................................................................................... 54
List of figures

Figure 3.1.1 : DWTP Llobregat-Abrera Process Flowsheet: Electrodialysis Reversal .......................................................... 12
Figure 4.2.1 : Electrodialysis process scheme .................................................................................................................. 14
Figure 4.2.2 : Reverse Osmosis function principle ............................................................................................................... 15
Figure 5.1.1 : flux distribution inside a fiber (show at air separation as an example) ............................................................. 18
Figure 5.1.2 : Schematic work principle of the desired membrane process ........................................................................ 19
Figure 5.2.1 : Measurable physical parameters for a system as it approaches equilibrium, starting from a conditions of only reactants and no products ........................................................................ 21
Figure 5.2.2 : Schematic diagram of flat sheet supported liquid membrane (FSSLM) in membrane separation process .................................................................................................................. 22
Figure 5.2.3 : Construction of a typical hollow fiber module ............................................................................................. 22
Figure 5.5.1 : Chemical structure of Aliquat® 336 .............................................................................................................. 24
Figure 5.5.2 : Separator filled with organic phase after shaking, aqueous phase already withdrawn into the beaker .......................................................................................................................... 26
Figure 5.5.3 : Silver nitrate titration apparatus .................................................................................................................. 27
Figure 5.5.4 : The evolution of electrical potential vs. the added volume during titration with AgNO3 after 1st washing .................................................................................................................... 29
Figure 5.5.5 : The plot of 1st derivative of electrical potential with respect to volume of silver nitrate ............................ 29
Figure 5.5.6 : Evolution of chloride division after the washing steps ................................................................................ 32
Figure 5.5.7 : Values for the equilibrium constant in each washing step .............................................................................. 34
Figure 5.5.8 : Updated evolution of chloride division after the washing steps ..................................................................... 35
Figure 5.5.9 : Overview about experimental obtained Keq values ....................................................................................... 36
Figure 5.5.10 : Flow-scheme of the Keq optimization calculation .......................................................................................... 39
Figure 5.5.11 : Comparison between experimental obtained and calculated equilibrium constant ............................... 40
Figure 5.6.1 : Schematic structure of a flat sheet membrane cell, feed phase left ..................................................................... 41
Figure 5.6.2 : Setup of FSSLM experiments as carried out in the lab .................................................................................. 42
Figure 5.6.3 : Compartments and membranes used for FSSLM experiments ........................................................................ 43
Figure 5.6.4 : Evolution of chloride concentration during the 100%v measurement ............................................................. 45
Figure 5.6.5 : Chloride evolutions plotted for various volume fractions of PTC mixture ..................................................... 45
Figure 5.6.6 : Scheme of the experimental set-up ................................................................................................................ 46
Figure 5.6.7 : Chloride concentration profile near and inside the liquid membrane .......................................................... 47
Figure 5.6.8 : Flow scheme of the chloride concentration trend line fitting ........................................................................ 51
Figure 5.6.9 : Process model applied to the 100 volume percentage membrane measurement ............................................ 52
Figure 5.6.10: Chloride evolution for 12.5%v measurement ............................................................................................... 53
Figure 5.6.11: Chloride evolution for 25%v measurement ................................................................. 53
Figure 5.6.12: Chloride evolution for 75%v measurement .................................................................. 53
Figure 5.6.13: Chloride evolution for 100%v measurement ................................................................. 53
Figure 5.7.1: Experimental setup of HFSLM process ........................................................................... 54
Figure 5.7.2: Experimental setup of the HFSLM experiment ............................................................... 55
Figure 5.7.3: Schematic chloride concentration profile as present around a fiber ................................. 56
Figure 5.7.4: Chloride concentration profile during the flow along a fiber ........................................... 57
Figure 5.7.5: Results of HFSLM experiments for different Aliquat® 336 volume percentages .......... 58
Figure 5.7.6: General velocity profiles in pipes for (a) laminar flow and (b) turbulent flow ................. 59
Figure 5.7.7: Flow scheme of the HFSLM experiments ................................................................. 59
Figure 5.7.8: Ion transport process in one single fiber .......................................................................... 60
Figure 5.7.9: Overview about the percentage chloride evolution for different concentrations of PTC .. 63
Figure 5.7.10: 25 %v HFSLM measurement ....................................................................................... 64
Figure 5.7.11: 50 %v HFSLM measurement ......................................................................................... 64
Figure 5.7.12: 75 %v HFSLM measurement ......................................................................................... 64
Figure 5.7.13: 100 %v HFSLM measurement ...................................................................................... 64
Figure 5.7.14: Equilibrium of carbonate compounds present in the feed phase ................................. 65
Figure 5.7.15: Equilibrium of carbonate compounds present in the stripping phase ......................... 66
Figure 5.7.16: recalculated 25 %v HFSLM evolution ................................................................. 69
Figure 5.7.17: recalculated 50 %v HFSLM evolution .......................................................................... 69
Figure 5.7.18: recalculated 75 %v HFSLM evolution .......................................................................... 69
Figure 5.7.19: recalculated 100 %v HFSLM evolution ....................................................................... 69
Figure 5.7.20: ln Korg – ln µ correlation plot ....................................................................................... 73
Figure 5.7.21: Plot of viscosity with respect to volume percentage of pure Aliquat® 336 in membrane.. 75
Figure 5.7.22: Correlation between %v of PTC used during the experiments and its corresponding pure values ......................................................................................................................... 76
Figure 5.8.1: Chloride evolution vs. the limit set by the EU; volume percentages of pure PTC .......... 77
Figure 5.8.2: Chloride evolution according to different initial conditions; in ppm chloride ............... 77
Figure 5.8.3: Chloride reduction rate with respect to different amounts of Aliquat® 336 ................. 78
Figure 5.9.1: Considering relevant parameters for the up–scaled version .......................................... 80
Figure 5.9.2: Schematic concurrent (left) and countercurrent concentration profiles ....................... 81
Figure 5.9.3: Schematic efficiency comparison between concurrent and countercurrent flow, shown exemplarily by reference to an heat exchanger ......................................................... 82
Figure 6.1.1: Treatment diagram including Electrodialysis Reversal Process ........................................ 83
Figure 6.2.1 : Scheme of concurrent flow modules ................................................................. 85
Figure 6.2.2 : Countercurrent flow module........................................................................ 86
Figure 6.5.1 : Pressure losses caused by one HFSLM module plotted against appropriate flows ........ 88
Figure 6.6.1 : Comparison of electricity cost to produce 1m^3 of clean water using competitive techniques ......................................................................................................................... 90
List of tables

Table 4.2.1.1 : Water classification according to its over – all salt content .................................................. 13
Table 5.5.2.1 : Aliquat® 336 specifications published by its reseller .............................................................. 25
Table 5.5.3.1 : The results of potentiometric measurements for 1st washing .................................................. 28
Table 5.5.3.2 : The results of potentiometric measurements for 1st washing .................................................. 31
Table 5.5.3.3 : Concentrations of all reactants after washing including the value for the equilibrium constant ................................ .......................................................... 34
Table 5.5.4.1 : Aliquat® 336 specifications published by BASF ........................................................................ 35
Table 5.5.4.2 : Final concentrations in state of equilibrium, including Keq ....................................................... 36
Table 5.5.4.3 : Calculated chloride concentration and MAPE estimation .......................................................... 39
Table 5.5.4.4 : Concentrations of all reactants based on calculated chloride concentrations .......................... 40
Table 5.6.3.1 : Measured chloride concentrations in feed cell during 100%v experiment .................................. 44
Table 5.6.4.1 : Values for membrane transport constant and error according to the optimization calculation .................................................................................................................. 52
Table 5.7.3.1 : Results of all the HFSLM experiments ................................................................................... 57
Table 5.7.4.1 : Values for membrane transport constant and error according to the optimization calculation .................................................................................................................. 62
Table 5.7.4.2 : Error observation according equilibrium constant recalculation .............................................. 67
Table 5.7.4.3 : Values for membrane transport constant and percentage error after the recalculation .... 68
Table 5.7.4.4 : Time measurements for viscosity .............................................................................................. 70
Table 5.7.4.5 : The results of the measurements of density of reactants .......................................................... 71
Table 5.7.4.6 : Viscosity measurements for lab temperature of about 21°C ....................................................... 72
Table 5.7.4.7 : Lookup table for the ln Korg – ln μ correlation ........................................................................... 73
Table 5.7.4.8: Viscosity measurement and Aliquat ® 336 concentration conversion ........................................ 74
Table 5.8.2.1: Calculation scheme for countercurrent flow .............................................................................. 82
1. Introduction

The project “Chloride reduction from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier” is part of the European Project Semester 2013 hosted by the Polytechnic University of Catalonia in Vilanova i la Geltru. It is one out of five projects, which are done in cooperation with commercial business and industries by international, interdisciplinary teams of four to six students.

The project is about investigating an alternative desalination technique called Hollow Fiber Supported Liquid Membrane (HFSLM) by carrying out several experiments in the laboratory. The aim is to develop a solution for the Abrera drinking water treatment plant that desalinates the water from the Llobregat river more efficient than the recently implemented electrodialysis reversal technique. If possible the solution should be applicable to an even higher concentration of salt and be able to desalinate all kinds of brackish water. A universal applicability would come along with numerous opportunities to sell the final product which makes it economic.

2. Water shortage

2.1. Freshwater

Freshwater is undoubtedly the most essential resource for any kind of life. While the amount of freshwater on earth remained quite constant, the demand for it constantly increases. Only three percent of the world’s water supply are freshwater, most of it is stored in glaciers and snowfields and less than one percent of it is accessible directly. That means that about 0.007 percent of the planet’s water is available as freshwater for mankind and it has to feed 6.8 billion people\(^1\). Nowadays already more than 1.3 billion people are suffering from water scarcity and its consequences – with an upward tendency.

2.2. What causes water shortage?

One of the main causes for water shortage is the uneven distribution of freshwater. While humid and semi humid areas are mostly not affected, arid and semi-arid areas are naturally threatened by water shortage since there is more evaporation than rainfall.

Another main cause is the exploding world’s population. A fairly constant amount of freshwater has to serve a growing population, a growing population on the other hand involves a widening of households, industries and agriculture, so that the demand for freshwater exponentially increases.

Increasing water pollution also causes water shortage, especially if the wastewater does not get treated. More than 90 percent of the world’s wastewater is not treated properly by a sewage treatment plant. In addition to this the climate change also has a significant influence on the water shortage problem due to the global warming and the involved fastened evaporation.

2.3. Consequences of water shortage

An insufficient provision with drinkable water can raise the chance to become diseased. Almost 80 percent of the diseases in poor countries are referable to polluted water. Water shortage not only has bad effects on the health, but also on the economy. Most industry sectors require a certain amount of water to produce their goods, especially the agricultural branch. This is particularly dramatic because a loss of agricultural production can cause a bottleneck of the food supply. Solving the problem of water shortage would therefore also bring a couple of positive side effects.

2.4. Basic approaches

There are three basic approaches to face the problem of water shortage:

First of all, Minimizing the use of fresh water. Manufacturing industries mostly use a huge amount of water to produce their goods. Building a car e.g. requires about 400000 liter, one kilogram of cheese 5000 liter\(^2\). The potential to decrease the amount of water needed is one possibility that has to be investigated in order to minimize the use of fresh water. The second option would be maximizing the supply for freshwater. A possible solution would be an artificial recharge of groundwater. Finally, the third approach is to optimize technologies for water treatment and water production. The project “Chloride reduction from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier” will address this approach by investigating a promising alternative water treatment technique called Hollow Fiber Supported Liquid Membrane.

3. Current situation in the Barcelona region

Barcelona as a metropolis located in the semi arid area of Catalonia is also not safe from water shortage. In 2008 Barcelona suffered from the worst drought for 60 years, they were forced to import emergency water to keep up the water supply\(^3\). As a consequence in 2009 new water treatment techniques such as ultrafiltration or reverse osmosis have been implemented to the system to avoid another bottleneck. With the Ter and the Llobregat rivers there are two main sources for freshwater which contribute about 85% of

\(^2\) http://www.vditz.de/fileadmin/media/publications/pdf/Wasserknappheit_Technologie_Band_76.pdf
\(^3\) http://www.guardian.co.uk/world/2008/may/14/spain.water
the whole water supply in the Barcelona metropolitan area, the last 15% come from groundwater resources. The level of salinity in the Llobregat river is above average (300-500 mg/l), not only because of naturally occurring sodium chloride deposits in the river basin geology, but also because of the potash mining industry located close to the river.

The Abrera drinking water treatment plant as one of two plants located along the Llobregat river feeds about 4.5 million people in the Barcelona metropolitan area. It is the largest desalination plant for urban supply in Europe⁴ and was awarded the “Desalination Plant of the Year” by Global Water Awards 2010⁵. Nevertheless there are two more water treatment plants, one is placed near Sant Joan Despi and also treats the water from Llobregat, the other one is placed in Cardedeu and treats the water from Ter.

3.1. The current drinking water treatment procedure in Abrera

The standard procedure in the Abrera drinking water treatment plant was extended 2009 with an electrodialysis reversal treatment (Fig. 3.1.1)

First the water is collected from the Llobregat river, sand and big solids are removed in the collecting zone. In order to oxidize several organic and inorganic compounds manganese permanganate is added afterwards. After a pre-chlorination the water is mixed and homogenized with a flocculating reagent and subsequently directed to the clarifiers, where the solids settle by precipitation and can be removed. Then the remaining sand is removed by various sandfilter and a major part of the organic pollutants is absorbed by a granular activated carbon bed (GAC).

---
⁴ http://www.gencat.cat/especial/prat/eng/que.htm
⁵ http://www.water-technology.net/projects/barcelonadesalination/
The following step is the recently implemented electrodialysis reversal treatment to reduce the salinity. Since the salinity only has to be reduced to a certain concentration set by the legislation of the European Union, the flow can be separated in order to treat the water more efficient.

Next the water is chlorinated in order to kill disease-causing bacterias that the water might contain. In the end the treated water is stored in one of four tanks with an overall capacity of 263,000 m³.

Optimizing the salinity reduction process by investigating an alternative technique is the main aim of the “Chloride Reduction” project.

4. Salinity

4.1. Definition

Salinity as one of many types of water pollution is defined as the dissolved salt content in water. Normally sodium chloride, also known as table salt, constitutes the major part of the water’s salinity and the chloride concentration is dependent on it. The maximum concentration of chlorides allowed in drinking water is set to 250mg/l by the legislation of the European Union (98/83/EC)⁷, which would be about 413mg/l of dissolved sodium chloride. Exceeding this value would on the one hand provide a salty taste to the water and on the other hand cause corrosion⁸. This is why not only drinking water but also process water has to be desalinated. Another reason is the increased rate of kettle tartar formations benefited by high chloride contents.

Based on the salinity there are three different kinds of water⁹:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>&lt; 0,5%</td>
</tr>
<tr>
<td>Brackish water</td>
<td>0,5% - 3,5%</td>
</tr>
<tr>
<td>Seawater</td>
<td>&gt; 3,5%</td>
</tr>
</tbody>
</table>

While seawater is only found in seas and oceans, sources for brackish and freshwater are numerous. Freshwater occurs on the earth’s surface in rivers, lakes and streams, as well as in any kind of ice and in the underground as groundwater. Brackish water on the other hand mostly appears in estuaries, where rivers stream into the open sea, but also in some seas or lakes. India for instance has the Chilika Lake, the

---

⁷ COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption
⁸ http://www.trinkwasserspezi.de/html/korrosion.html
⁹ http://www.abendblatt.de/ratgeber/wissen/article1792589/Wie-ist-Brackwasser-definiert.html
world’s largest brackish water lake, and since India has a constantly increasing demand for drinking water it is desirable to develop a solution for desalination that is able to handle all kinds of brackish water.

4.2. Common techniques of desalination

The two most common techniques to desalinate brackish water are reverse osmosis on the one hand and electrodialysis on the other hand.

4.2.1. Electrodialysis

In 1952 Ionics, a young company that is nowadays owned by General Electric Company, revealed its newest invention - Electrodialysis with salt transfer membranes - the first truly practical and economical technique to desalinate brackish water\(^\text{10}\). The basic work principle of electrodialysis is to generate a DC field on a stack of flat sheet ion exchange membranes arranged in a cation – anion configuration that pulls the salts that have to be removed across the membranes (Fig. 4.2.1). The result is desalinated water, the product, on the one hand and a recirculating concentrated saline water flow on the other hand.

![Electrodialysis process scheme](http://origin-ars.els-cdn.com/content/image/1-s2.0-S0011916413000738-gr2.jpg)

In 1974 electrodialysis reversal (EDR) was introduced as an improved replacement for the conventional electrodialysis. It eliminates the need to feed chemical substances such as acids to scale off salts from the membranes, because the DC field was alternatingly reversed which makes the scale off process occurring automatically. In fact, this is one of the major advantages of electrodialysis reversal over reverse osmosis.

\(^{10}\) [http://www.gewater.com/pdf/Technical%20Papers_Cust/Americas/English/TP1038EN.pdf]

\(^{11}\) [http://origin-ars.els-cdn.com/content/image/1-s2.0-S0011916413000738-gr2.jpg]
The Abrera drinking water treatment plant also uses EDR to desalinate the water after an extensive pretreatment.

**4.2.2. Reverse Osmosis**

While the reverse osmosis process was first observed in 1748 it took more than 200 years to commercialize it for practical purposes. The reverse osmosis process requires a semi-permeable membrane and a pump to increase the pressure which is needed to force water from a saline solution through a semi-permeable membrane (Fig. 4.2.2). Since most of the dissolved salts are kept in the initial solution, its concentration further increases, while the product water on the other side can be considered as desalinated.

![Figure 4.2.2 : Reverse Osmosis function principle](http://www.hitachi.com/environment/showcase/solution/industrial/images/img_desalination/09.jpg)

The higher the concentration of dissolved salts in the feedwater, the higher the energy input to compensate the naturally increased osmotic pressure. Therefore a part of the brine solution is withdrawn from time to time. During the 80s the reverse osmosis also has undergone major improvements. The development of thin-film-composite membranes enabled a more consistent salt rejection, a substantially reduced operating pressure and the need for acid in the feedwater to prevent scaling was eliminated\(^\text{13}\).

---


\(^{13}\) http://www.oas.org/dsd/publications/Unit/oea59e/ch20.htm
4.2.3. Purpose of membrane techniques

The membrane technology covers the process engineering not without a reason. It has several advantages, from which the following are the most important ones:

- They operate without additional heating thus they have a really low energy consumption
- They are capable of provide separation of azeotropics and isomorphics crystallization products, as it is impossible to conduct this using distillation of recrystallization due to the heat required
- They easily support the filtration of macromolecules or particles in case of water treatment (e.g. Ultrafiltration for swimming pools)
- They are broadly used in medicine – as a artificial kidneys or lungs. They are able to provide bubble-free supply of oxygen to blood or remove toxic substances in case of damage of kidney or too high concentration of toxins in the blood.

Ongoing research in material science and further process technology improvements lead to a significant development in the last decades and this trend is predicted to continue driven by even stricter environmental regulations, new innovations, additional applications as well as rapidly increasing water demand in developing regions. Due to all these factors the global demand of new high – tech membranes is expected to grow by around 8% annually in the upcoming years. With Chemical processing and water treatment as the main fields of application the worldwide market was valued at approximately US$15.6 billion in 2012 and is expected to reach US$25 billion by 2018\textsuperscript{14}. Since North America and Western Europe remain the key leaders for membrane systems because of their recent innovations and developments the membrane market promises huge potential.

\textsuperscript{14} “Market Report: Global Membrane Technology Market”, Acmite Market Intelligence, March 2013
5. Experimental part

5.1. General work principle

The technique we have investigated is a specialized application of membrane technology, which covers all procedural processes of substance transport between two fractions by using permeable membranes. In general, this method is used for mechanical separation from gaseous or liquid streams using technical membranes. The most common appliance for this is reverse osmosis. In comparison to conventional thermal separation processes like distillation or crystallization this separation technique is purely physical and does not required special heat treatment, what makes the membrane technology less energy-intensive and points out its particular advantage. Providing water suppliers with this opportunity of tremendous energy savings the membrane technology is becoming increasingly important. With the help of Ultra-/Microfiltration it is possible to remove particles, colloids and macromolecules, so that river and even waste as well as brackish water can be disinfected in this way.

To describe the mass transfer through a membrane, two basic models can be used: The solution-diffusion model and the hydrodynamic model. As really common in scientific issues these models do not exclude each other, instead both transport mechanisms can certainly occur side by side in real membranes. The hydrodynamic model describes the mass transfer as a transport through pores, in the simplest case purely due to convection. This requires the size of the pores to be smaller than the diameter of the to separate components. Particles with a diameter bigger than the diameter of the pores are hold back and remain as filter cake. This working principle is mostly used in micro- and ultrafiltration to remove macromolecules and colloids from solutions and dispersions. The first principle is quite well known by most of the people, but membranes can also function according to another mechanism.

The solution-diffusion model defines the transport through the membrane as an effect of diffusion. The particles which need to pass through the membrane have to get dissolved in the membrane first before they are able to be transported. This model is more relevant for dense membranes without a high number of natural pores. During the separation process more and more molecules of the same species are dissolved in the membrane and transported to the other side because of the upcoming concentration gradient inside the membrane, which initializes the diffusion process. Afterwards the transported particles get back – extracted at the other side of the membrane, which is better known as stripping in chemical terminology. This reduction of these molecules on the outer surface of the membrane forms a boundary layer with another concentration gradient which is created by molecules which cannot pass through the membrane.

Despite which principle dominates the mass transfer, there are two main flow configurations of membrane applications: cross – flow and dead – end filtration. Using the dead – end constellation the
fluid “flow” is oriented normally to the membrane surface and stopped by it, whereas the feed flows tangentially to the membrane surface in cross – flow arrangement. Hereby the filtrate is removed from the same side further downstream and the permeate flow can be withdrawn from the opposite side of the membrane. Flat sheet membranes for dead – end appliances are easy to fabricate but processes with this flow geometry can only be carried out as batch processes. The use of cross – flow oriented membranes is much higher, but therefore they offer the opportunity to run a continuous separation process. The most common constructive form for this kind of membranes are hollow fiber modules. They consist of an assembly of self-supporting fibers with dense skin separation layers, which are supported by a more open matrix helping to withstand pressure gradients and maintain structural integrity. For such modules it is not uncommon to contain up to 10 000 fibers. The diameter of the fibers can differ a lot and varies from around 200 \( \mu \text{m} \) up to over 2500 \( \mu \text{m} \) and depends on the final use of the membrane module. The main advantage of hollow fiber modules is the very large surface area within an enclosed volume, what increases the efficiency of separation processes.

Figure 5.1.1 : flux distribution inside a fiber (show at air separation as an example)

Considering the driving force of a membrane separation process it is possible to distinguish several different types of membrane operations. The three most important categories are pressure driven (micro- and ultrafiltration, reverse osmosis, …), electric potential gradient driven (electrodialysis, …) and concentration driven operations. Due to the fact that reverse osmosis as a pressure driven application is characterized by a high consumption of electricity by pumps to reach appropriate pressure levels, our technique is based on the concentration gradient as the main driving force in order to even minimize this disadvantage and to improve the sustainability of water treatment and desalination processes.

Working with a Supported Liquid Membrane (SLM) the chloride ions reduction process is chiefly carried out according to the solution-diffusion model introduced above: The excess chloride ions from the water, 

\[\text{http://upload.wikimedia.org/wikipedia/commons/2/25/Flux_distribution_inside_the_fiber.jpg}\]
which has to be treated (feed phase), are dissolved in the organic phase of the liquid membrane. This organic phase contains an ionic liquid, which molecules act as the carrier to transport these ions to the other side of the membrane. Having arrived there the chloride is back – extracted to the stripping phase. The back extraction is the same process like the former extraction, just carried out vice versa.

Supported liquid membranes (SLM) are based on the use of porous solid membranes (mostly polymeric) which support or hold an organic liquid inside and separate the feed and the stripping aqueous solutions. The pores of such a membrane are completely filled with organic liquid which also contains some carrier molecules, enforced by capillarity. This impregnation process makes the membranes relatively stable and heterogeneous, unaffected if prepared as a flat-sheet membrane or a hollow-fiber. In general, the solids supports are made out of hydrophobic material, which facilitates wetting by the organic solution and the rejection of aqueous phases.

The ionic liquid is used as a carrier inside the liquid membrane to ensure a thorough transport possibility for the injected chloride ions. An ionic liquid can be described as a salt in a liquid state which is characterized by a large fraction of ions and short – lived ion pairs in comparison to most of ordinary liquids like water or kerosene which consist mostly out of electrically neutral molecules. In our investigation process, a widely known ionic liquid, was used. Its carrier properties are caused by its structure which is outweighed dominated by one chloride anion which can easily be replaced by almost any other anion.

This procedure of an ordinary ionic exchange represents the fundamental idea of our transport process through the membrane: Chloride ions are extracted from the feed and build transportable compounds with the Aliquat® 336 molecules. Due to an increasing concentration of this Aliquat® 336 – chloride complex at the feed – membrane interface the concentration gradient inside the membrane increases as well and this compound is transported to the other side of the membrane in order to establish an

Figure 5.1.2 : Schematic work principle of the desired membrane process
homogeneous concentration level over the whole membrane. In interaction with the bicarbonate anion at the membrane – stripping interface the chloride ion is set free and replaced by bicarbonate which is afterwards transported to the feed phase. Generally speaking, an ion transportation circle such as seen in Figure 5.1.2 gets established.

To make this process useful the volume of stripping used during the process has to be much smaller than the volume of feed, otherwise the chloride contamination would just get translocated. But by transferring the chloride to a smaller volume two advantages can be achieved: The volume of polluted water decreases and, second, the concentration of chloride in the stripping phase will be much higher than in the feed what might make it useful to use this brine for salt production.

5.2. Investigation strategy

As mentioned above our idea to reduce the concentration of chloride from brackish water by hollow fiber supported liquid membranes (HFSLM) using ionic liquids as a carrier consists of three major sub – processes:

- Extraction of the chloride ions from the feed phase
- Diffusion of the Aliquat® 336 – chloride compound through the membrane
- Back – extraction to the stripping phase

In order to find a well – fitting model for the overall transfer mechanism it was necessary to explore each step so as to obtain all the characteristic parameters which dominate each step of the separation process. This procedure was required to be able to predict the performance of the whole hollow fiber module at the end of the experiments and to carry out a knowledgeable up – scaling calculation for industrial use.

The Extraction and Stripping process is a chemical reaction which can be described with the following equation:

$$\text{Aliq}^+\text{HCO}_3^{−}\text{org} + \text{Cl}^{−}_{\text{aq}} \leftrightarrow \text{Aliq}^+\text{Cl}^{−}_{\text{org}} + \text{HCO}_3^{−}_{\text{aq}}$$  \hspace{1cm} (1)

As it can be seen in the formula this reaction is able to be carried out into both directions. This phenomenon is called “chemical equilibrium” in scientific jargon and is characterized by a continuously ongoing forth and back reaction. This special kind of chemical reactions never stops and the reagents from the left side of the equation are transformed into the products on the right all the time. But simultaneously these products are also converted into the reactants on the left again. The rates of forward and reverse reaction is thereby controlled by the relation of the concentrations of all the reactants in the chemical system: At the beginning the forth reaction will dominate the whole process because of the absence of reaction products, but with an increasing concentration of them also the back reaction is
enforced increasingly which seems to lower the forward reaction rate. In fact the absolute reaction rate of the forth reaction stays constant and only the apparent reaction rate shrinks due to the progressive reconversion of the reaction products. The point, at which the reaction seems to stand still, because both reaction speeds are equal, is called “chemical equilibrium” and can be calculated using the equilibrium constant, which is specific for each chemical reaction system.

![Diagram](image)

**Figure 5.2.1:** Measurable physical parameters for a system as it approaches equilibrium, starting from a conditions of only reactants and no products

Therefore it was necessary to detect the equilibrium constant of the reaction shown above in order to be able to make precise predictions which percentage of the contained chloride is really extracted from the feed to the membrane and later on to the stripping phase.

After having obtained this specific reaction value we started with the real membrane transport experiments. To get a first impression how our idea works out, we started to investigate the chloride reduction process using **Flat Sheet Membranes (FSM)**. This procedure has several advantages:

- Flat sheet membranes are much cheaper than a hollow fiber module, just in case our idea would have been totally wrong
- Experiments with flat sheet membranes are less work intensive and support nevertheless enough data for a first membrane transport process evaluation
- The mathematical and chemical model behind this process is much easier than the one which is required for hollow fibers, nonetheless this flat sheet model can be expanded for hollow fiber calculations afterwards easily what approved this step by step investigation

---

Finally we did experiments with a **Hollow Fiber Module (HF)** on lab scale to adapt our former achievements to the kind of membrane, which would also be applied for industrial use afterwards. After considering some last changes in our model we were able to calculate an up – scaled version of our technology.

5.3. **Phase transfer catalyst - Aliquat ® 336**

Phase transfer catalysis (PTC) is a special form of heterogeneous catalysis, what means that catalyst and reactants are not present in the same phase or even not in the same state of matter. The PTC facilitates the transport of a reactant from one phase into another through a phase which could not be passed without these carrier molecules. So is chloride easily soluble in an aqueous phase but insoluble in an organic one in the absence of the phase transfer catalysts. That is the reason why an ionic carrier is

---


needed to enable chloride to migrate through the organic SLM which separates feed and stripping phase from each other.

Aliquat® 336, known as Stark’s catalyst, is a hydrophobic anionic liquid, quaternary ammonium salt and a mixture of octyl and decyl chains which offers good attributes as a phase transfer catalyst. The choice of Aliquat 336® was imposed by our supervisors, but anyway, it is one of the best choices for single-ion transfer carrier because of the following reasons:\(^{19}\):

- It is cheap
- It is easy to be used by unqualified personnel, as:
  - It is not highly volatile, whereas the majority of another PTC’s are
  - It is chemically and thermally stable
  - It is almost solid, what supports easy handling and chemical operation
- Created salts inside are not soluble, thus they precipitate and may be easily filtered out

The transportation mechanism through the membrane is affected by two properties of the PTC: the concentration and the viscosity. The higher the concentration the more chloride molecules can be transferred at the same time. But on the other hand a higher concentration of 336 also affects a higher viscosity of the organic phase inside the membrane due to its relatively high viscosity what has a negative influence on the velocity of the Aliquat® 336. Therefore it is necessary to investigate various Aliquat® 336 mixtures with different concentrations in order to obtain the best relation between these two contrary features in the sense of efficiency of the chloride transport.

### 5.4. The bicarbonate anion

Sodium bicarbonate (NaHCO\(_3\)) is a slightly basic salt used in our experiment as an aqueous solution for replacing chloride anions (Cl\(^-\)) with bicarbonate anion (HCO\(_3\)\(^-\)). It is able to substitute Cl\(^-\) anions in the Aliquat – molecule and enforces the chloride transportation thereby.

For our project NaHCO\(_3\) has numerous advantages:

- It is cheap – the price for laboratory requirements is about 20 €/kg, whereas the purchasing price for industry is much lower with only – 0.2 €/kg
- It is easy to use
- It is possible to create wide range of mixture concentration due to high solubility
  
  (10.3g NaHCO\(_3\) / 100g H\(_2\)O)

---

\(^{19}\) Jyri-Pekka Mikkola, Pasi Virtanen, Rainer Sjöholm, „Aliquat 3361—a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids“, International Journal of Chemical Engineering Volume 2012 (2012)
• As a powder it is a stable and non-toxic compound, due to which it does neither require qualified personnel nor special equipment to be used
• Instead it even has a good effect on human health: It reduces acidity of dietary components, has prevention effects on dental cavities, reduces muscle fatigue and provides a more stable acid-base balance
• It does not increasing the blood pressure, in comparison to sodium chloride

However, sodium bicarbonate has as well some disadvantages:

• It is quite sensitive to pH – value changes, what might affect the binding possibilities for chloride anions to the Aliquat® 336 structure, what might result in some experimental error
• Since sodium bicarbonate is used to replace chloride ions so as to reduce their concentration to fulfill the drinking water standard set by the EU, it is essential to introduce some limitations of its molar concentration in the mixture used for washing – out chloride anions in order to minimize the amount of needed sodium bicarbonate to keep possible costs as low as possible

5.5. Equilibrium investigation and preparation of the phase transfer catalyst

5.5.1. Background

This initial step in our whole investigation process was needed because of two reasons: As already mentioned this experiment helped to determine the state of chemical equilibrium of the balance extraction reactions we were looking at. On the other hand, in the condition as it is sold, contains itself a high fraction of chloride ions as it is composed of a large organic cation associated with a chloride anion as shown below.

Figure 5.5.1: Chemical structure of Aliquat® 336

![Chemical structure of Aliquat® 336](image)

20 Aliquat® 336 datasheet, BASF, February 2012
Since the following FSM and HF experiments should deliver truthful data about the transportation process through the membrane, we considered it as useful to change the chloride ions in the Aliquat® 336 for bicarbonate at the beginning of all our experiments. This measure does not affect the transport mechanism at all owing to the balance reaction which final state of equilibrium is not influenced by its initial conditions. But lowering the chloride concentrations inside the membrane minimizes the sources for experimental errors when measuring the chloride concentration evolutions in the feed and the stripping cell because the possibility of releasing additional chloride ions from the used Aliquat® 336 can almost be precluded.

For industrial scale this fact is not relevant and this initial procedure can be skipped due to much bigger volumes used, though in lab scale this influence should be minded, especially while working with really small samples and relatively low chloride concentrations in the flat sheet modules.

5.5.2. Procedure

First of all, the organic phase with its certain amount of ionic liquid as carrier has to be prepared. In our experiments we worked with 20 volume percentages of in a decanol / kerosene mixture to ensure thorough impregnation of the solid organic membrane. Without these organic solvents this might lead to a problem because of Aliquat® 336’s quite polar behavior. The chemical specifications of the used Aliquat® 336 according to the datasheet delivered by its supplier are shown in table 2.5.2.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>404.17 g/mol</td>
</tr>
<tr>
<td>Purity</td>
<td>89.5 - 91.0 %</td>
</tr>
<tr>
<td>Density</td>
<td>0.898 g/cm³</td>
</tr>
</tbody>
</table>

Furthermore a sodium bicarbonate solution was needed to wash out chloride anions from Stark’s catalyst.

1. To prepare the Aliquat® 336 solution, following reagents were mixed:
   - 100 ml of Aliquat® 336
   - 50 ml of Decanol
   - 350 ml of kerosene
   The obtained mixture was a viscous, yellow fluid.

---

21 Aliquat® 336 product specification, Alfa Aesar, January 2011
2. In order to prepare the solution of NaHCO$_3$, 2 liters of bdistilled water were mixed with 151.2g of solid sodium bicarbonate. Afterwards the solution was heated in order to obtain better solubility of the solvent.

Afterwards the whole Aliquat ® 336 mixture was put into a separator together with 500ml of bicarbonate solution. After that, the separator has been put into a mechanical shaker for 20 minutes in order to perform the ion exchange, which reaction is as follows:

\[
\text{Aliq}^+\text{Cl}_{\text{org}}^- + \text{HCO}_3^{-\text{Aq}} \leftrightarrow \text{Aliq}^+\text{HCO}_3^{-\text{org}} + \text{Cl}_{\text{Aq}}^-
\] (2)

The next step was to separate the two phases again in order to remove the aqueous phase and to measure its amount of out washes chloride ions. These two steps have been repeated several times to gain enough data to evaluate the equilibrium constant of the chemical reaction shown above. The phrase “washing” is used to illustrate the procedure we were using, but actually a real chemical reaction has taken place all the time.

In order to determine the chloride concentration in the aqueous phase the common method of potentiometric measuring was used: Into a beaker filled with approximately 50ml of specifically bidistilled water (free of chloride anions) a small volume sample of aqueous phase was poured. Then, 2ml of concentrated nitric acid was added to acidify the environment. Afterwards the potentiometric measurements accompanying titration with silver nitrate has been conducted.
The basic principle of this procedure is to measure the electrical potential of the solution and to figure out the point of highest sensibility, which highlights the inflection point of the measured solution and indicates the moment when all the chloride ions are bound by silver ions as formulated with formula (3). Silver chloride is almost not soluble in water and flocculates. By measuring the added volume of silver nitrate and knowing its concentration the present concentration of chloride in the aqueous phase can be obtained.

\[
 Cl^{-}_{Aq} + Ag^{+}_{Aq} \rightarrow AgCl_{s}
\]  

(3)

The measurement results are presented exemplarily for the 1st washing. The results of all the washings will be put in a table at the end of this section.

### 5.5.3. Results

The inflection points were found by careful manual titration basing on the value of the derivative \( \frac{dE}{dv} \). For the first washing step this point is highlighted in grey in the table below.
Table 5.5.3.1: The results of potentiometric measurements for 1st washing

<table>
<thead>
<tr>
<th>AgNO₃ volume [ml]</th>
<th>Potential [mV]</th>
<th>dE / dv</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>181.2</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>190.2</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>204.9</td>
<td>14.7</td>
</tr>
<tr>
<td>2.08</td>
<td>206.5</td>
<td>20</td>
</tr>
<tr>
<td>2.24</td>
<td>210</td>
<td>21.875</td>
</tr>
<tr>
<td>2.32</td>
<td>211.9</td>
<td>23.75</td>
</tr>
<tr>
<td>2.4</td>
<td>214</td>
<td>26.25</td>
</tr>
<tr>
<td>2.48</td>
<td>216.3</td>
<td>28.75</td>
</tr>
<tr>
<td>2.56</td>
<td>218.9</td>
<td>32.5</td>
</tr>
<tr>
<td>2.64</td>
<td>221.5</td>
<td>32.5</td>
</tr>
<tr>
<td>2.72</td>
<td>224.7</td>
<td>40</td>
</tr>
<tr>
<td>2.8</td>
<td>227.5</td>
<td>35</td>
</tr>
<tr>
<td>2.88</td>
<td>232.6</td>
<td>63.75</td>
</tr>
<tr>
<td>3</td>
<td>240.4</td>
<td>65</td>
</tr>
<tr>
<td>3.08</td>
<td>247.3</td>
<td>86.25</td>
</tr>
<tr>
<td>3.16</td>
<td>256.4</td>
<td>113.75</td>
</tr>
<tr>
<td>3.2</td>
<td>262.2</td>
<td>145</td>
</tr>
<tr>
<td>3.24</td>
<td>269.4</td>
<td>180</td>
</tr>
<tr>
<td>3.28</td>
<td>278.1</td>
<td>217.5</td>
</tr>
<tr>
<td>3.32</td>
<td>288.4</td>
<td>257.5</td>
</tr>
<tr>
<td><strong>3.36</strong></td>
<td><strong>299.1</strong></td>
<td><strong>267.5</strong></td>
</tr>
<tr>
<td>3.4</td>
<td>308.7</td>
<td>240</td>
</tr>
<tr>
<td>3.44</td>
<td>316.6</td>
<td>197.5</td>
</tr>
</tbody>
</table>

The inflection point outlines the maximum of the electrical potential sensibility referred to the added volume of silver nitrate as shown in Figure 5.5.5 and characterizes hence the turning point in the plot of potential against volume.
Based on the data obtained from the first washing and the appropriate potentiometric measurements it is possible to calculate the concentration of chloride anions in the withdrawn aqueous phase according to the reaction equation number (2). The concentration of AgNO₃ was equal to 0.0199 M and the volume needed for binding all chloride anions in a 0.4 ml sample of added aqueous phase was 3.36 ml. According
to the stoichiometric factors of this reaction the concentration of the contained amount of chloride – ions can be evaluated as follows:

\[ [Cl^-] = \frac{0.0199 \ [M] \cdot 3.36 \ [ml]}{0.4 \ [ml]} = 0.167 \ [M] \]

Knowing the initial concentration of chloride anions in the used Aliquat® 336 solution it is possible to determine the decrease in its concentration after washing. The initial concentration of chloride anions in the Aliquat® 336 solution are calculated based on the information provided by Alfa Aesar as a licensed reseller.

In our experiments a mixture of 100ml of Aliquat® 336, 50ml of decanol and 350ml of kerosene was used. To determine the concentration of chloride anions in the Aliquat® 336, its molecular weight, its purity, its density and the used volume were needed. As the purity is not exactly given, we calculated with the approximate value of 0.9.

\[ m_{Aliq} = 0.9 \cdot 0.898 \left( \frac{g}{cm^3} \right) \cdot 100 \ [cm^3] = 80.82 [g] \]

\[ n_{Aliq} = \frac{80.82 [g]}{404.17 \ [g/mol]} = 0.199966 \ [mol] = 0.2 \ [mol] \]

\[ [Aliq - Cl] = \frac{0.2 \ [mol]}{0.5 \ [dm^3]} = 0.4 \ [M] \]

This quantity indicates the initial concentration of chloride-ions in the Aliquat® 336 phase and is marked as \([Aliq - Cl]_0\).

Now, having all this data and referring to the primary chemical equation number (1) again,

\[ Aliq - Cl_{org} + HCO_3^{-}_{aq} \leftrightarrow Aliq - HCO_3_{org} + Cl^{-}_{aq} \]

we can use our experimental obtained values of the concentration of chloride-ions in the aqueous phase after each washing step to calculate the concentrations of all the remaining reactants.

According to our prepared solution of sodium bicarbonate, the Aliquat® 336 mixture is washed with, the initial concentration of NaHCO₃ in the aqueous-phase is 0.9 M.

\[ c_i = \frac{n_i}{V_{solution}} = \frac{m_i}{M_i \cdot V_{solution}} = \frac{m_i}{M_i \cdot V_{sol}} \]

\[ c_{NaHCO_3} = \frac{m_{NaHCO_3}}{M_{NaHCO_3} \cdot V_{sol}} = \frac{151.2 [g]}{84.007 \ [g/mol] \cdot 2 [l]} = 0.8999 \ [mol/l] = 0.9 \ [M] \]
This initial concentration of sodium bicarbonate is constant for all the washing due to the fact that the aqueous phase is completely replace after each step. For the same reason the concentration of chloride ions before every single washing procedure is zero. In relation to the chemical equation, our experiment is based on, the determined concentration of out washed chloride-ions by each washing is equal to the decrease in the concentration of \([\text{Aliq-Cl}]\) in the organic phase. The mass balance, set up for the whole amount of Aliquat® 336 in the system, provides us with the last required equation. In the following, all relations are shown as formulas. The index \(i\) indicates to the number of the washing and all the concentrations refer to the state of equilibrium after the washing process.

\[
[Cl^-]_i \quad \text{measured chlorid concentration in aqueous phase after each washing}
\]

\[
[HCO_3^-]_i = [HCO_3^-]_0 - [Cl^-]_i
\]

\[
[\text{Aliq-Cl}]_i = [\text{Aliq-Cl}]_{i-1} - [Cl^-]_i
\]

\[
[\text{Aliq-HCO}_3]_i = [\text{Aliq-Cl}]_0 - [\text{Aliq-Cl}]_i
\]

The following tabled gives an overview about all the washing procedures and the amounts of chloride having been washed out in each step. At the bottom the accumulated removed chloride fraction can be seen as well as its remaining part in the organic phase. This table is visualized in Figure 5.5.6. [Aliquat] initial represents the initial concentration of Aliquat® 336 in the organic mixture and acc [Cl] stands for the over-all amount of out-washed chloride after the appropriate number of washings.

<table>
<thead>
<tr>
<th>WASHING</th>
<th>V sample [ml]</th>
<th>VAgNO3 [ml]</th>
<th>([\text{Cl}^-]), M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>aqueous phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>3.6</td>
<td>0.16712</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3.92</td>
<td>0.07799</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>4.28</td>
<td>0.04258</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>3.64</td>
<td>0.02414</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>4.12</td>
<td>0.01639</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>3.96</td>
<td>0.01125</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>3.26</td>
<td>0.00649</td>
</tr>
<tr>
<td>8</td>
<td>18</td>
<td>3.68</td>
<td>0.00407</td>
</tr>
<tr>
<td>9</td>
<td>40</td>
<td>5.12</td>
<td>0.00255</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>1.64</td>
<td>0.00163</td>
</tr>
<tr>
<td>sum out-washed</td>
<td></td>
<td></td>
<td>0.35420</td>
</tr>
<tr>
<td>remaining</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5.3.2: The results of potentiometric measurements for 1st washing
Knowing all these concentrations for every single washing process we can calculate the constants of equilibrium. This constant is the characteristic value of every reversible chemical reaction and specific for each chemical system (in the sense of combination of reactants). Its value supplies an impression where the state of equilibrium is located. The higher this constant the higher is the concentration of products at the end whereas small values describe the final equilibrium more on the left side of the chemical reaction. High and low values can only be distinct relatively because there is no fixed definition and the magnitude of this constant can vary a lot, but it is always positive.

For a general balance reaction like

$$a \text{A} + b \text{B} + c \text{C} + \cdots \Rightarrow p \text{P} + q \text{Q} + r \text{R} + \cdots$$

the equilibrium constant is defined as

$$K_x = \frac{x(\text{P})^p \cdot x(\text{Q})^q \cdot x(\text{R})^r \cdots}{x(\text{A})^a \cdot x(\text{B})^b \cdot x(\text{C})^c \cdots}$$

*capital letters ... chemical reactants*

*small letters ... stoichiometric coefficient*

*K ... equilibrium constant*

*x ... concentrations in the state of equilibrium*

The value of the equilibrium constant of a chemical reaction is influenced by environmental condition such as temperature or pressure, but unaffected by the initial concentration relation of the reactants in this chemical system.
According to equation (2) the present equilibrium constant of our extraction reaction can be formulated as follows

\[ K = \frac{([\text{Aliq} - \text{HCO}_3^-]_{\text{org}} \cdot [\text{Cl}^-]_{\text{aq}})}{([\text{Aliq} - \text{Cl}^-]_{\text{org}} \cdot [\text{HCO}_3^-]_{\text{aq}})} \]

To obtain this major reaction defining parameter for the first washing the procedure is like this:

The initial concentration of [Aliq-Cl] was equal to round about 0.4 M and the concentration of bicarbonate anions is constantly 0.9 M at the beginning of each washing step. The result of the measurement of the [Cl] concentration in the aqueous phase sample was determined with 0.167 M.

The amount of chloride having been removed from the organic phase has to be equal to the amount of bicarbonate which has been added to Aliquat 336. The reason for that is the replacement of Cl by HCO$_3^-$.

\[ [\text{Cl}^-]_1 = 0.167 \text{ M} \]
\[ [\text{HCO}_3^-]_1 = [\text{HCO}_3^-]_0 - [\text{Cl}^-]_1 = 0.9 \text{ M} - 0.167 \text{ M} = 0.733 \text{ M} \]
\[ [\text{Aliq} - \text{Cl}]_1 = [\text{Aliq} - \text{Cl}]_0 - [\text{Cl}^-]_1 = 0.4 \text{ M} - 0.167 \text{ M} = 0.233 \text{ M} \]
\[ [\text{Aliq} - \text{HCO}_3]_1 = [\text{Aliq} - \text{Cl}]_0 - [\text{Aliq} - \text{Cl}]_1 = 0.4 \text{ M} - 0.233 \text{ M} = 0.167 \text{ M} \]

\[ K_1 = \frac{([\text{Aliq} - \text{HCO}_3^-]_1 \cdot [\text{Cl}^-]_1)}{([\text{Aliq} - \text{Cl}^-]_1 \cdot [\text{HCO}_3^-]_1)} = \frac{(0.167 \cdot 0.167)}{(0.233 \cdot 0.733)} \left[ \frac{M^2}{M^2} \right] = 0.1633 \]

By replacing the aqueous phase before every washing, the initial concentrations of chloride and bicarbonate ions are always 0 M respectively 0.9 M like here. In contrast the organic phase remains for all the washings which causes that the conditions of the Aliquat ® 336 mixture after every washing outline the starting conditions for the following one. Applying this procedure to all the experimental data results in the following overview about our investigational obtained value for the equilibrium constant $K_{eq}$. 

33
Table 5.5.3.3: Concentrations of all reactants after washing including the value for the equilibrium constant

<table>
<thead>
<tr>
<th>WASHING</th>
<th>[Cl⁻]</th>
<th>[Aliq-HCO₃]</th>
<th>[Aliq-Cl]</th>
<th>[HCO₃]</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0</td>
<td>0</td>
<td>0.40000</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.16712</td>
<td>0.1671</td>
<td>0.23288</td>
<td>0.7329</td>
<td>0.16364</td>
</tr>
<tr>
<td>2</td>
<td>0.07799</td>
<td>0.2451</td>
<td>0.15489</td>
<td>0.8220</td>
<td>0.15014</td>
</tr>
<tr>
<td>3</td>
<td>0.04258</td>
<td>0.2877</td>
<td>0.11232</td>
<td>0.8574</td>
<td>0.12719</td>
</tr>
<tr>
<td>4</td>
<td>0.02414</td>
<td>0.3118</td>
<td>0.08818</td>
<td>0.8759</td>
<td>0.09746</td>
</tr>
<tr>
<td>5</td>
<td>0.01639</td>
<td>0.3282</td>
<td>0.07178</td>
<td>0.8836</td>
<td>0.08483</td>
</tr>
<tr>
<td>6</td>
<td>0.01125</td>
<td>0.3395</td>
<td>0.06053</td>
<td>0.8887</td>
<td>0.07103</td>
</tr>
<tr>
<td>7</td>
<td>0.00649</td>
<td>0.3460</td>
<td>0.05404</td>
<td>0.8935</td>
<td>0.04647</td>
</tr>
<tr>
<td>8</td>
<td>0.00407</td>
<td>0.3500</td>
<td>0.04997</td>
<td>0.8959</td>
<td>0.03180</td>
</tr>
<tr>
<td>9</td>
<td>0.00255</td>
<td>0.3526</td>
<td>0.04743</td>
<td>0.8975</td>
<td>0.02109</td>
</tr>
<tr>
<td>10</td>
<td>0.00163</td>
<td>0.3542</td>
<td>0.04580</td>
<td>0.8984</td>
<td>0.01405</td>
</tr>
</tbody>
</table>

Figure 5.5.7: Values for the equilibrium constant in each washing step

5.5.4. Conclusion

Due to a relatively constant environment in the lab over the whole period of our experiments the obtained equilibrium constant of our reaction should be almost steady. Yet figure 2.5.3.4. illustrates quite obvious the opposite. Of course, the measured results were affected by experimental errors, but taking into account the evolutions shown in figure 2.5.3.3. as well, some mismatches in the Aliquat ® 336
properties seemed most likely: With progressive extraction processes the concentration of \([\text{Aliq} - \text{Cl}]\) should shrink down to zero, however in our system this limit appears earlier.

Having consulted BASF, the owner of the registered trademark Aliquat® 336 and the one and only producer of this chemical, our suspicion got proofed: The molecular weight of Aliquat® 336 is 442 g / mol instead of 404.17 g / mol as incorrectly labeled by its reseller Alfa Aesar.

<table>
<thead>
<tr>
<th>Table 5.5.4.1 : Aliquat® 336 specifications published by BASF</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>442 g/mol</td>
</tr>
<tr>
<td>Purity</td>
<td>90.4 %</td>
</tr>
<tr>
<td>Density</td>
<td>0.88 g/cm³</td>
</tr>
</tbody>
</table>

These new information lead to a different initial concentration of \([\text{Aliq} - \text{Cl}]\) with only round about 0.36 M in the organic phase which influenced all further calculations. Consistent with our expectations the concentration of chloride bound to Aliquat® 336 was then constantly decreasing to zero and on the other hand the accumulated amount of removed chloride strived towards the initial concentration of Aliquat® 336. The following diagram illustrates this fact.

![Diagram](image)

Figure 5.5.8 : Updated evolution of chloride division after the washing steps

By recalculating all the affected concentrations an improved reflection of the chemical process and its equilibrium constant was obtained.

---

22 Aliquat® 336 datasheet, BASF, February 2012
Table 5.5.4.2: Final concentrations in state of equilibrium, including Keq

<table>
<thead>
<tr>
<th>WASHING</th>
<th>[Cl-]</th>
<th>[Aliq-HCO3]</th>
<th>[Aliq-Cl]</th>
<th>[HCO3]</th>
<th>Keq</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0</td>
<td>0</td>
<td>0.35996</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.16712</td>
<td>0.1671</td>
<td>0.19284</td>
<td>0.7329</td>
<td>0.19761</td>
</tr>
<tr>
<td>2</td>
<td>0.07799</td>
<td>0.2451</td>
<td>0.11486</td>
<td>0.8220</td>
<td>0.20247</td>
</tr>
<tr>
<td>3</td>
<td>0.04258</td>
<td>0.2877</td>
<td>0.07228</td>
<td>0.8574</td>
<td>0.19763</td>
</tr>
<tr>
<td>4</td>
<td>0.02414</td>
<td>0.3118</td>
<td>0.04814</td>
<td>0.8759</td>
<td>0.17852</td>
</tr>
<tr>
<td>5</td>
<td>0.01639</td>
<td>0.3282</td>
<td>0.03175</td>
<td>0.8836</td>
<td>0.19181</td>
</tr>
<tr>
<td>6</td>
<td>0.01125</td>
<td>0.3395</td>
<td>0.02049</td>
<td>0.8887</td>
<td>0.20979</td>
</tr>
<tr>
<td>7</td>
<td>0.00649</td>
<td>0.3460</td>
<td>0.01401</td>
<td>0.8935</td>
<td>0.17930</td>
</tr>
<tr>
<td>8</td>
<td>0.00407</td>
<td>0.3500</td>
<td>0.00994</td>
<td>0.8959</td>
<td>0.15989</td>
</tr>
<tr>
<td>9</td>
<td>0.00255</td>
<td>0.3526</td>
<td>0.00739</td>
<td>0.8975</td>
<td>0.13534</td>
</tr>
<tr>
<td>10</td>
<td>0.00163</td>
<td>0.3542</td>
<td>0.00576</td>
<td>0.8984</td>
<td>0.11166</td>
</tr>
</tbody>
</table>

Figure 5.5.9: Overview about experimental obtained Keq values

Evident from table 2.5.4.2 as well as the graph above there is still a lack of constancy in the equilibrium constants obtained during our experiments. According to chemical laws this is not possible and instead the measurements have to fulfill the following equation.

\[ K_1 = K_2 = \ldots = K_{eq} \]
On this understanding a “recalculation” of the expected out washed chloride concentrations for every single washing was the next step in order to receive a constant value for $K_{eq}$. This mathematical problem is only recursive solvable and is based on the equation for the equilibrium constant already shown above:

$$K_{eq} = \left( \frac{[\text{Aliq} - HCO_3^-]_{\text{org}} \cdot [Cl^-]_{\text{aq}}}{([\text{Aliq} - Cl^-]_{\text{org}} \cdot [HCO_3^-]_{\text{aq}}) \right)$$

First of all it is necessary to express all concentrations in the state of equilibrium (index 2) in relation of their starting concentrations (index 1) for every washing step (index i). Therefore the generalized terms from our calculations example for the first washing can be used.

$$K_{eq} = \frac{(([\text{Aliq} - HCO_3^-]_1 + [Cl^-]_2) \cdot [Cl^-]_2)}{(([\text{Aliq} - Cl^-]_1 - [Cl^-]_2) \cdot ([HCO_3^-]_1 - [Cl^-]_2))}$$

In order to eliminate excess chemical values two further simplifications can be used.

$$[\text{Aliq} - HCO_3^-]_1 = [\text{Aliq} - Cl^-]_0 - [\text{Aliq} - Cl^-]_1$$

$$[HCO_3^-]_1 = [HCO_3^-]_0 = 0.9 \, M$$

Putting all these considerations together the following equation can be received:

$$K_{eq} = \frac{(([\text{Aliq} - Cl^-]_0 - [\text{Aliq} - Cl^-]_1) + [Cl^-]_2) \cdot [Cl^-]_2)}{(([\text{Aliq} - Cl^-]_1 - [Cl^-]_2) \cdot ([HCO_3^-]_0 - [Cl^-]_2))}$$

By means of this relation the concentration of the chloride ions in the aqueous phase in washing number $i$ can be obtained by using known initial concentrations and the concentration of Aliq-Cl from the former washing $i-1$ which has already been evaluated. Starting with washing number one this allows calculating all required values by using only initial concentrations at the beginning.

Finding an explicit expression for $[Cl^-]_2$ leads to a quadratic equations which can be solved using the so called “monic form” as shown below

$$0 = (1 - K_{eq}) \cdot [Cl^-]_2^2 + ([\text{Aliq} - Cl^-]_0 - [\text{Aliq} - Cl^-]_1 + K_{eq} \cdot ([\text{Aliq} - Cl^-]_1 + [HCO_3^-]_0)) \cdot [Cl^-]_2 - ([HCO_3^-]_0 \cdot K_{eq} \cdot [\text{Aliq} - Cl^-]_1)$$

$$[Cl^-]_{21/2} = -\frac{p}{2} \pm \sqrt{\left(\frac{p}{2}\right)^2 - q}$$

with
Due to the fact that every second order equation has two possible solutions, some limits for possible values of \([Cl]_2\) have to be introduced. According to chemical laws and logical understanding concentrations can never be negative (the same is valid for \(K_{eq}\)) and therefore only positive solutions should be accepted. By estimating the equations for \(p\) and \(q\) it is obvious that \(p\) is always positive: The numerator is more or less a sum of concentrations which is definitely positive due to positive summands and the term \((1-K_{eq})\) in the denominator should be positive as well, being owed to our experimental values in the area 0,2\(\pm\)0,05.

For this reason the first term of the “monic equation” is negative and positive values for the chloride concentrations can only be obtained by addition. As a result the “monic solution” is reduced to only one solution.

\[
[Cl^-]_{i2} = -\frac{p}{2} + \sqrt{\left(\frac{p}{2}\right)^2 - q}
\]

Using the method of the mean absolute percentage error (MAPE) the accuracy of this method for constructing fitted series values can be evaluated. It usually expresses accuracy as a percentage, and is defined by the formula:

\[
MAPE = \frac{100\%}{n} \sum_{t=1}^{n} \left| \frac{A_t - F_t}{A_t} \right|
\]

where \(A_t\) is the actual value and \(F_t\) is the forecasted value.

The difference between \(A_t\) and \(F_t\) is divided by the Forecast value \(F_t\) again. The absolute value in this calculation is summed for every fitted or forecasted point in time and divided again by the number of fitted points \(n\). Multiplying by 100 makes it a percentage error.

The advantage of this procedure is that each measured concentration is weighted with the same amount during the fitting process. This is necessary because of the constantly decreasing total quantity of out washed chloride in progressive washings. Without regarding this percentage distribution the fitted points of the last washings might differ by several hundred percent from the measured ones without being noticed.
After implementing this technique in Excel the Macro-Solver can be used to minimize the value of this error by verifying the value of \( K_{eq} \). The result is a well fitted series of chloride concentrations in combination with an appropriate constant result for the equilibrium constant.

The next part gives an overview about all the data which has been discussed above together with a well fitted calculated concentration evolution model.

Table 5.5.4.3 : Calculated chloride concentration and MAPE estimation

<table>
<thead>
<tr>
<th>washing</th>
<th>[Cl(^-)] in [M]</th>
<th>difference [Cl(^-)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>measured</td>
<td>calculated</td>
</tr>
<tr>
<td>1</td>
<td>0.16712</td>
<td>0.17088</td>
</tr>
<tr>
<td>2</td>
<td>0.07799</td>
<td>0.07786</td>
</tr>
<tr>
<td>3</td>
<td>0.04258</td>
<td>0.04270</td>
</tr>
<tr>
<td>4</td>
<td>0.02414</td>
<td>0.02529</td>
</tr>
<tr>
<td>5</td>
<td>0.01639</td>
<td>0.01559</td>
</tr>
<tr>
<td>6</td>
<td>0.01125</td>
<td>0.00982</td>
</tr>
<tr>
<td>7</td>
<td>0.00649</td>
<td>0.00628</td>
</tr>
<tr>
<td>8</td>
<td>0.00407</td>
<td>0.00404</td>
</tr>
<tr>
<td>9</td>
<td>0.00255</td>
<td>0.00262</td>
</tr>
<tr>
<td>10</td>
<td>0.00163</td>
<td>0.00170</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By minimizing the mean absolute percentage error of the chloride evolution in the aqueous phase the following equilibrium constant was obtained:
$K_{eq} = 0.21180$

Table 5.5.4.4: Concentrations of all reactants based on calculated chloride concentrations

<table>
<thead>
<tr>
<th>WASHING</th>
<th>[Cl⁻]</th>
<th>[Aliq-HCO₃]</th>
<th>[Aliq-Cl]</th>
<th>[HCO₃]</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0</td>
<td>0.35996</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.170880</td>
<td>0.1709</td>
<td>0.18908</td>
<td>0.7291</td>
</tr>
<tr>
<td>2</td>
<td>0.077861</td>
<td>0.2487</td>
<td>0.11122</td>
<td>0.8221</td>
</tr>
<tr>
<td>3</td>
<td>0.042696</td>
<td>0.2914</td>
<td>0.06853</td>
<td>0.8573</td>
</tr>
<tr>
<td>4</td>
<td>0.025291</td>
<td>0.3167</td>
<td>0.04324</td>
<td>0.8747</td>
</tr>
<tr>
<td>5</td>
<td>0.015586</td>
<td>0.3323</td>
<td>0.02765</td>
<td>0.8844</td>
</tr>
<tr>
<td>6</td>
<td>0.009824</td>
<td>0.3421</td>
<td>0.01783</td>
<td>0.8902</td>
</tr>
<tr>
<td>7</td>
<td>0.006276</td>
<td>0.3484</td>
<td>0.01155</td>
<td>0.8937</td>
</tr>
<tr>
<td>8</td>
<td>0.004043</td>
<td>0.3525</td>
<td>0.00751</td>
<td>0.8960</td>
</tr>
<tr>
<td>9</td>
<td>0.002618</td>
<td>0.3551</td>
<td>0.00489</td>
<td>0.8974</td>
</tr>
<tr>
<td>10</td>
<td>0.001701</td>
<td>0.3568</td>
<td>0.00319</td>
<td>0.8983</td>
</tr>
</tbody>
</table>

Figure 5.5.11: Comparison between experimental obtained and calculated equilibrium constant
5.6. Flat Sheet Supported Liquid Membrane (FSSLM) experiments

5.6.1. Background

In this next stage of our experimental investigation a number of experiments with FSSLM were conducted. This was necessary due to two main reasons: On the one hand this approach lead on to a first over – all impression of our desired transport process and on the other hand the mathematical model of such a dead – end membrane geometry appliance is much easier to obtain than an appropriate one for cross – flow arrangements, however it can be seen as preparation for this as it can be modified afterwards to fulfill this second implementation quite readily.

![Figure 5.6.1: Schematic structure of a flat sheet membrane cell, feed phase left](image)

The flat sheet supported liquid membrane is the simplest form of the liquid membrane. The solid support is impregnated with the organic phase containing PTC’s and is clamped between two half cells using gaskets thus forming two compartments as shown in Figure 5.6.1. One compartment is for feed solution and the other compartment contains the stripping phase. Both the phases are stirred by mechanical stirrers.

---

23 Guerra Millán, Francisco José; Michel, Andrea (2007). “Membrandiffusion”, “Bericht für das Praktikum Chemieingenieurwesen I WS06/07”
Corresponding to the value $K_{eq}$ the chloride ions from the feed phase interact with the organic phase of the membrane and are partly removed from the aqueous phase. Because of this an imbalance of the chloride concentration in the membrane occurs which leads to diffusional movement of $[\text{Aliq} - \text{Cl}]$ – particles to the other site of the membrane in order to recondition homogeneity. Arrived at the other site these molecules start to react with the aqueous phase in the stripping cell get back extracted. The extraction processes on both sites of the membrane can be modeled by using $K_{eq}$ from the former experiments. The only remaining unknown value is the constant of transport according to Fick’s law of diffusion inside the membrane.

In comparison to similar balance processes, such as known from heat transfer, this procedure does not stop when equal concentration levels are reached in both cells: The main driving force of this transport mechanism is the high initial concentration of bicarbonate (adjusted to 0.9 M in our experiments) in the stripping solution which is almost 50 times as high as the initial concentration used for chloride (round about 0.02 M, which is an appropriate value to simulate the current contamination of brackish water here in the El Llobregat region). This high gradient in the bicarbonate concentration causes that almost all the chloride ions are extracted from the feed and transported to the membrane – stripping phase interface where they are back – extracted almost completely according to local chemical equilibrium. This results in an continuous chloride concentration gradient inside the membrane accompanied by ongoing diffusion to the stripping phase far beyond an equal concentration level in both cells. Summarizing, the much higher amount of bicarbonate used for the ionic interchange with chloride as well as the state of the chemical equilibrium, the whole process is based on, enable this procedure to reduce the chloride concentration in the feed almost to zero.

### 5.6.2. Procedure
Our experiment consisted of two cells with a flat membrane in between. One of the cells, the so called stripping cell, was filled with an aqueous solution of sodium bicarbonate and the other one, the feed cell, with a mixture of sodium chloride. By filling the second cell, the chemical process of chloride reduction from the feed cell was initiated. Subsequently the evolution of the chloride concentration was determined. Therefore the feed phase was sampled and measured at certain times. In order to avoid unnecessary experimental errors, a solution of approximately the same volume and concentration as the taken sample was given back to the feed cell all the time after measuring each sample.

These experiments were conducted with a volume of 210 ml both for feed and stripping phase. As feed phase a solution of 1 g sodium chloride per liter of bidistilled water was used. The stirring apparatuses were adjusted to round about 1100 turns per minute to ensure thorough mixing in the cells.

The used flat sheet membranes are composed of polyethylene supported by a Teflon mesh. At the beginning of the experiments these membranes were impregnated with Aliquat ® 336 mixtures of different concentrations. This procedure helps to find a relation between the velocity of the chloride reduction and the amount of phase transfer carrier molecules in the organic phase.

The used Aliquat ® 336 mixture was the one we produced during our washing processes. Thus the maximum concentration of PTC is limited by approximately 0.36 M.

5.6.3. Results

The results of these measurements are shown below exemplarily for the membrane which was prepared with 100 volume percent of out washed Aliquat ® 336 mixture.
Table 5.6.3.1: Measured chloride concentrations in feed cell during 100%v experiment

<table>
<thead>
<tr>
<th>measurement</th>
<th>time</th>
<th>chloride concentration in feed cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in h</td>
<td>molar</td>
</tr>
<tr>
<td>initial</td>
<td>0.000</td>
<td>0.0171633</td>
</tr>
<tr>
<td>1</td>
<td>1.933</td>
<td>0.0143693</td>
</tr>
<tr>
<td>2</td>
<td>5.417</td>
<td>0.0115753</td>
</tr>
<tr>
<td>3</td>
<td>8.083</td>
<td>0.0074507</td>
</tr>
<tr>
<td>4</td>
<td>10.500</td>
<td>0.0052687</td>
</tr>
<tr>
<td>5</td>
<td>14.083</td>
<td>0.0031133</td>
</tr>
<tr>
<td>6</td>
<td>22.500</td>
<td>0.0009779</td>
</tr>
<tr>
<td>7</td>
<td>26.500</td>
<td>0.0007344</td>
</tr>
<tr>
<td>8</td>
<td>30.750</td>
<td>0.0003592</td>
</tr>
<tr>
<td>9</td>
<td>40.500</td>
<td>0.0001437</td>
</tr>
<tr>
<td>10</td>
<td>51.083</td>
<td>0.0000559</td>
</tr>
<tr>
<td>11</td>
<td>57.500</td>
<td>0.0000160</td>
</tr>
</tbody>
</table>

The abbreviation “ppm” stands for “parts per million” and characterizes one millionth of a certain value, what is used as a pseudo unit in science and engineering to describe small values of various dimensionless quantities. It is widely common to use this notation for concentration units such as mole or mass fractions, since these variables are quantity – per – quantity measures and hence pure numbers without associated units. Due to the fact that water has a density of

$$\rho_{H2O} = \frac{1}{l} \cdot \frac{g}{ml}$$

concentrations values in mol / l can be subscribed into mol / kg without further calculations. Therefore the conversion from M to ppm is as easy as follows, considering that

$$V_{solution} \approx V_{H2O}$$

what presents a suitable approximation for our purpose.

$$c_{Cl^-} = \frac{n_{Cl^-}}{V_{H2O}} \Leftrightarrow c_{Cl^-} = \frac{n_{Cl^-}}{m_{H2O}} \Leftrightarrow c_{Cl^-} = \frac{n_{Cl^-} \cdot M_{Cl^-}}{m_{H2O}}$$

The unit relation of the last concentration expression (mass fraction) is already dimensionless and its value in ppm is obtained according to this calculation

$$\left[ \frac{mol \cdot g}{mol \cdot l} \right] = \left[ \frac{g}{kg} \right] \cdot 1000 \left[ \frac{mg}{g} \right] = \left[ \frac{mg}{kg} \right] = 10^{-6} = \left[ ppm \right]$$
The constantly shrinking percentage concentration as shown in Figure 5.6.4. is an indicator for the effectiveness of this method. After one and a half day the concentration of chloride ions was almost decreased to zero. This result matched with our expectations.

Figure 5.6.4 : Evolution of chloride concentration during the 100%v measurement

The higher the concentration of phase transfer catalyst inside the membrane the higher is the velocity of the transport process. This behavior is highlighted in Figure 5.6.5 and fulfills our expectations likewise.

Figure 5.6.5 : Chloride evolutions plotted for various volume fractions of PTC mixture

5.6.4. Conclusions

The measurement supplied a quite good impression of the process and underlined our expectations. Nevertheless this data is influenced by experimental errors which have to be reduced to a minimum by
means of modeling the transport mechanism based on chemical and physical laws minding all three involved steps: extraction, diffusion and stripping.

Extraction and stripping are regulated by the equilibrium constant $K_{eq}$ which was already obtained. Due to the fact that the stripping process works vice versa than the process investigated during the washing experiments the value of this constant is equal to its reciprocal.

$$\text{Aliq}^+\text{Cl}^-_{\text{org}} + \text{HCO}_3^-_{\text{aq}} \rightarrow \text{Aliq}^+\text{HCO}_3^-_{\text{org}} + \text{Cl}^-_{\text{aq}} \quad \text{observed reaction direction during washings}$$

$$\text{Aliq}^+\text{HCO}_3^-_{\text{org}} + \text{Cl}^-_{\text{aq}} \rightarrow \text{Aliq}^+\text{Cl}^-_{\text{org}} + \text{HCO}_3^-_{\text{aq}} \quad \text{desired reaction direction for extraction}$$

$$K_{eq} = \frac{([\text{Aliq} - \text{Cl}^-]_{\text{org}} \cdot [\text{HCO}_3^-]_{\text{aq}})}{([\text{Aliq} - \text{HCO}_3^-]_{\text{org}} \cdot [\text{Cl}^-]_{\text{aq}})} = \frac{1}{K_{eq}}$$

Another fact we have to consider is the inhomogeneity of concentrations in both cells. “Far” away from the membrane concentrations are almost stable but near the surface concentration gradients as shown in Figure 5.6.7 occur based on both the withdrawal of chloride and the influx of bicarbonate. According to the boundary layer theory, well known from other physical and chemical problems, this gradient is locally limited to a certain area near the membrane surface and its diameter can be decreased by applying forced convection. In order to minimize the size of these boundary layers we adjusted our stirring systems at a high number of revolutions, what permitted us not to take account of the boundary layer and to approximate the concentration as constant all over the cells. This procedure allowed us to use the

---

measured concentration values in the feed cell to calculate the concentration of \([\text{Aliq} – \text{Cl}]\) in the membrane at the feed – membrane interphase (index 1).

![Diagram of chloride concentration profile near and inside the liquid membrane]

**Figure 5.6.7**: Chloride concentration profile near and inside the liquid membrane

The diffusion process of \([\text{Aliq} – \text{Cl}]\) through the membrane is controlled by Fick’s law of diffusion, which relates the diffusive flux to the concentration of the participating substances under the assumption of steady state. The flux is postulated to go from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient.

\[
J = -D \frac{dc}{dx}
\]

where

- \(J\) is the “diffusional flux” in \(\frac{kmol}{s \cdot m^2}\)
- \(D\) is the diffusion coefficient or diffusivity in \(\frac{m^2}{s}\)
- \(c\) is the concentration in \(\frac{mol}{l}\)
- \(x\) is the position inside the membrane in \(m\)

For our experiment the diffusional flux can be expressed as molar flux of chloride alternatively bicarbonate through the membrane. As we are only interested in the flux across the membrane and not in its profile inside we can change this differential equation for increments.
Defining a new constant as the transport constant of the membrane $K_{org}$

$$K_{org} = \frac{D}{\Delta x}$$

the initial equation can be expressed as

$$J = -K_{org} \cdot (c_2 - c_1)$$

what leads to the following relation for concretely our system:

$$J = K_{org} \cdot ([Aliq - CI]_1 - [Aliq - CI]_2)$$

The new introduced transport constant of the organic liquid membrane is only depended on membrane characteristics such as porosity, thickness and tortuosity and the liquid it is impregnated with.

The diffusion process is followed by the back – extraction of the transported chloride ions, which are replaced by bicarbonate from the stripping phase. Hence this step is defined by the “original” equilibrium constant.

To determine the evolution of chloride in the feed cell (index f) it is necessary to solve the mass balance for Cl\(^-\) in this cell.

\[ \text{input} - \text{output} + \text{production} = \text{accumulation} \] (4)

Input and production can be set equal to zero because there is no possibility for chloride to be transported from the stripping to the feed due to its initial concentration of 0 M in there. Production can be passed over since there is no chemical reaction generation further chloride taking place in the whole system. So the initial balance gets simplified to

\[ \text{output} = \text{accumulation} \]

Accumulation identifies the change of the amount of substance of chloride ions in the feed at any time as \(\frac{dn_f}{dt}\). Consequently this value is equal to the amount that is transported through the membrane, defined as the output N.

\[ \frac{dn_f}{dt} = -N \]
Since mol can be expressed as the product of concentration and volume:

\[ Vf \cdot \frac{d[Cl^-]_f}{dt} = -N \]

The amount of substance of chloride transported through the membrane (N) can be connected with the molar flux as follows, where A is the transference area

\[ Vf \cdot \frac{d[Cl^-]_f}{dt} = -J \cdot A_{\text{trans}} \]

\[ Vf \cdot \frac{d[Cl^-]_f}{dt} = -K_{\text{org}} \cdot A \cdot \left( [\text{Aliq} - Cl]_1 - [\text{Aliq} - Cl]_2 \right) \quad (5) \]

Based on \( K_{eq} \) and the extraction process \([\text{Aliq} - Cl]_1 \) and \([\text{Aliq} - Cl]_2 \) can be determined as functions of the concentrations of \([Cl^-] \) and \([HCO_3^-] \) in the feed (f) respectively in the receiving (s) cell as:

\[ [\text{Aliq} - Cl]_1 = \frac{[Cl^-]_f \cdot [\text{Aliq} - HCO_3]_1}{K_{eq} \cdot [HCO_3^-]_f} \]

and

\[ [\text{Aliq} - Cl]_2 = \frac{[Cl^-]_s \cdot [\text{Aliq} - HCO_3]_2}{K_{eq} \cdot [HCO_3^-]_s} \]

Taking into account that the entire amount of Aliquat ® 336 is constant in the membrane over the whole process, the concentration of \([\text{Aliq} - HCO_3] \) can be expressed as

\[ [\text{Aliq}] \; \text{ini} = \text{const.} = [\text{Aliq} - Cl] + [\text{Aliq} - HCO_3] \]

\[ [\text{Aliq} - HCO_3] = [\text{Aliq}] \; \text{ini} - [\text{Aliq} - Cl] \]

Applying this to the previous equations reduces the number of variables what leads to equations which are soluble knowing the concentrations in the cells. Starting with the initial conditions in each cell the evolution of \([\text{Aliq} - Cl] \) at points 1 and 2 can be calculated recursively.

\[ [\text{Aliq} - Cl]_1 = \frac{[Cl^-]_f \cdot ([\text{Aliq}] \; \text{ini} - [\text{Aliq} - Cl]_1)}{K_{eq} \cdot [HCO_3^-]_f} = \frac{[Cl^-]_f \cdot [\text{Aliq}] \; \text{ini}}{[Cl^-]_f + K_{eq} \cdot [HCO_3^-]_f} \]

\[ [\text{Aliq} - Cl]_2 = \frac{[Cl^-]_s \cdot ([\text{Aliq}] \; \text{ini} - [\text{Aliq} - Cl]_2)}{K_{eq} \cdot [HCO_3^-]_s} = \frac{[Cl^-]_s \cdot [\text{Aliq}] \; \text{ini}}{[Cl^-]_s + K_{eq} \cdot [HCO_3^-]_s} \]
Using a fixed value for the membrane transport constant $K_{org}$ and the two equations shown above the molar transport $N$ can be evaluated which leads, connected to the mass balance equation, to the theoretical evolution of chloride in the feed cell. Therefore equation (5) is modified:

$$V_f \cdot \frac{d[Cl^-]_f}{dt} = -K_{org} \cdot A \cdot ([Aliq - Cl]_1 - [Aliq - Cl]_2)$$

$$V_f \cdot ([Cl^-]_f(t + \Delta t) - [Cl^-]_f(t)) = -K_{org} \cdot A \cdot ([Aliq - Cl]_1 - [Aliq - Cl]_2) \cdot \Delta t$$

Due to the exchange of one bicarbonate ion for one chloride ion the mass balance for [HCO$_3$] is similar. The only difference is the increasing concentration of bicarbonate in the feed instead of a decrease. This little change is realized by inverting the algebraic sign on the right side of the equation:

$$V_f \cdot ([HCO_3^-]_f(t + \Delta t) - [HCO_3^-]_f(t)) = +K_{org} \cdot A \cdot ([Aliq - Cl]_1 - [Aliq - Cl]_2) \cdot \Delta t$$

To relate the concentrations in the feed cell with the concentrations of the stripping cell a global balance for both kinds of ions has to be established:

$$V_{feed} \cdot [Cl^-]_{initial} = V_{feed} \cdot [Cl^-]_{feed} + V_{strip} \cdot [Cl^-]_{strip} + V_{organic} \cdot [Aliq - Cl]$$

Assuming that $V_{organic}$ is much smaller than $V_{feed}$ and $V_{strip}$ as well as that the concentration of chloride is really low because of the former out–washing experiment, the balance can be rewritten as.

$$V_{feed} \cdot [Cl^-]_{initial} = V_{feed} \cdot [Cl^-]_{feed} + V_{strip} \cdot [Cl^-]_{strip}$$

The same could be done for bicarbonate. Since our experiment was carried out with equal volumes for feed and stripping, the balance can be written as a simple sum of concentrations.

$$[Cl^-]_{initial} = [Cl^-]_{feed} + [Cl^-]_{strip}$$

Accordingly, knowing the [Cl] evolution in the feed cell, the evolution of chloride in the stripping cell can be determined as well. This procedure is adaptable for the [HCO$_3$] evolution.

Summarizing all the considerations and formulas above, a set of four first order differential equations has to be solved in order to calculate the FSSLM experiments as a whole chemical system and to predict the evolutions off all the reactants in the system:
As this system of differential equations is not solvable analytically, it was implemented in MATLAB in order to be solved numerically using the well-known Runge–Kutta–Algorithm.

The strategy to find best-fitting calculated concentration evolutions was to predict chloride concentration trends according to preset but variable values for $K_{org}$. Based on its numerically integrated evolution, the MATLAB script evaluated the mean absolute percentage error of the calculated trend at the appropriate sampling times compared to the measured values. The underlying figure of $K_{org}$ was changed by a minimization loop in order to obtain this particular value which leads to a minimal MAPE error.

![Flow scheme of the chloride concentration trend line fitting](image)

**Figure 5.6.8**: Flow scheme of the chloride concentration trend line fitting

<table>
<thead>
<tr>
<th>Feed cell</th>
<th>chloride</th>
<th>$V_f \cdot \frac{dc_{Cl,f}}{dt} = - K_{org} \cdot A \cdot ( [Aliq - Cl]_1 - [Aliq - Cl]_2 )$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bicarbonate</td>
<td>bicarbonate</td>
<td>$V_f \cdot \frac{dc_{HCO_3,f}}{dt} = + K_{org} \cdot A \cdot ( [Aliq - Cl]_1 - [Aliq - Cl]_2 )$</td>
</tr>
<tr>
<td>Stripping cell</td>
<td>bicarbonate</td>
<td>$V_s \cdot \frac{dc_{HCO_3,s}}{dt} = - K_{org} \cdot A \cdot ( [Aliq - Cl]_1 - [Aliq - Cl]_2 )$</td>
</tr>
<tr>
<td>chlorine</td>
<td>chlorine</td>
<td>$V_s \cdot \frac{dc_{Cl,s}}{dt} = + K_{org} \cdot A \cdot ( [Aliq - Cl]_1 - [Aliq - Cl]_2 )$</td>
</tr>
</tbody>
</table>
The MATLAB script, we developed as the basis of this optimization calculation, can be found in the appendix. The obtained results are shown below.

![Figure 5.6.9](image-url)

**Figure 5.6.9** : Process model applied to the 100 volume percentage membrane measurement

<table>
<thead>
<tr>
<th>%v Aliquat ® 336</th>
<th>12.5%</th>
<th>25%</th>
<th>50%</th>
<th>87.5%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{org} ) in m/min</td>
<td>2.111328e-005</td>
<td>1.835938e-005</td>
<td>1.757813e-005</td>
<td>1.207031e-005</td>
<td>1.120117e-005</td>
</tr>
<tr>
<td>MAPE in %</td>
<td>1.9648</td>
<td>1.3654</td>
<td>2.9067</td>
<td>10.8522</td>
<td>13.2352</td>
</tr>
</tbody>
</table>

The variable \( K_{org} \) was introduced as a real material constant which is not affected by the state of the transportation process. This definition does not match with the data shown in Table 5.6.4.1. A reason for the decreasing values can be found in the increasing viscosity of the membrane liquid correspondent to the ascending volume percentage of Aliquat ® 336. This consideration is intensified by the relatively high error values of the 87.5% and 100% measurements which differ a lot from the rest. Nevertheless a further investigation of this observation was not necessary, even though this point was regarded later on during the hollow fiber measurements, because its crucial purpose was fulfilled by proving our main idea of possible chloride transport using supported liquid membranes. The model for the flat sheet membranes can already be seen as a preparation for the next experiments because in hollow fibers the concentrations
of feed and stripping solution are not constant along the membrane due to flowing but the occurring process of ion movement is the same.

Summarizing the following graphs point out the correlation between velocity of chloride concentration decrease and the different volume percentages of Aliquat ® 336 in the membranes.

Figure 5.6.10: Chloride evolution for 12.5%v measurement

Figure 5.6.11: Chloride evolution for 25%v measurement

Figure 5.6.12: Chloride evolution for 75%v measurement

Figure 5.6.13: Chloride evolution for 100%v measurement
5.7. Hollow fiber Supported Liquid Membrane (HFSLM) experiments

5.7.1. Background

The next step and most important part of the project itself was the investigation of chloride concentration reduction in a HFSLM module in lab scale. Since the membranes in such modules are arranged in cross-flow position they are able to extract chloride from the flushed through feed phase continuously instead of only batch operation as found in the flat sheet setup. By the help of continuous flows through the module the settling of particles at the membrane surface is reduced what extends both the lifetime and the efficiency of these membranes in comparison to dead-end processes due to a decreased fouling rate. These advantages make this technique particular interesting for industrial use and underline the necessity of a precisely investigation of its transport phenomenon.

The outer cell of the module is made out of a single nonporous material through which the solution, present inside, cannot be transported. Inside the shell, many thin fibers are packed in neat rows. In the present case the stripping phase passed through the fibers and the feed phase through the shell side by the help of gear pumps. But of course, this flow constellation can be chosen according to the purpose.

Figure 5.7.1: Experimental setup of HFSLM process

5.7.2. Procedure

The HFSLM experiments consisted of two major parts: membrane preparation and the chloride concentration measurement itself.

The preparation of the HFSLM was necessary in order to measure the chloride evolution for several different concentrations of carrier inside the liquid membrane. Therefore the replacement of the organic phase from the former experiment was essential and done like this:

According to the desired volume percentage of PTC in the liquid membrane (25 %v, 50 %v, 75 %v and 100 %v) an appropriate volume of the very initial washed out Aliquat ® 336 mixture was given to a corresponding amount of a 10 %v decanol – 90 %v kerosene mixture in order to obtain 200 ml organic phase in general.

50 ml of this mixture were withdrawn afterwards and saved for the proper measurements due to reasons mentioned further below.

Afterwards the apparatus has been started with 300 ml of bidistilled water in the feed and 150 ml of sodium bicarbonate solution in the stripping reservoir. After adding the remaining 150 ml of organic mixture and starting the stirring system so as to produce a thorough emulsion the pressure in the apparatus has be reduced to its minimum what leads to a pressure difference of about 0.3 bar between the stripping tube – and the feed shell – side. Subsequently this pressure gradient forces the organic liquid through the hollow fibers. Having received at least 100 ml of organic phase in the feed beaker the replacement of “old” liquid can be seen as completed due to the empirically obtained volume of organic liquid which sticks inside the fibers of about 50 ml.

Figure 5.7.2 : Experimental setup of the HFSLM experiment
The last step was washing the module several times with bicarbonate solution and bidistilled water to ensure the module being free of chloride residues and organic phase which is not stuck in membrane.

The experimental investigation itself proceeded quite similar:

In comparison to the FSSLM process the volumes of feed and stripping were not equal any more but chosen with a relation of 10 : 1 to approach our measurements to the finally required conditions: 5 l of bidistilled water in the feed phase were washed with 0.5 l of sodium bicarbonate stripping solution. Considering the hold – up volumes in the module, 400 ml of bicarbonate solution and 4720 ml of water were put in the apparatus. Due to fact that as a result of the steady flow small volumes of organic phase might get pulled out of the membrane the restrained 50 ml of organic mixture were added to the stripping so as to replace these possibly losses which is import for supplying membrane stability.

![Figure 5.7.3: Schematic chloride concentration profile as present around a fiber](image)

The feed phase was carried shell – side with an adjusted pressure difference of 0.2 bar compared to the stripping shell – side. This supports the chloride transport and prevents that organic particles might get pushed into the to cleaned water. Both the flows were set to 5 l / h.

After stabilization of the process, the measurements of chloride concentration were done by sampling at different times using titration with AgNO₃, like in case of previous experiments with flat sheet membranes. After taking each sample a proper amount of 1000 ppm chloride and distilled water was added to maintain volume and concentration equilibrium.
Sampling has been conducted every several minutes or hours, dependently on the process. Under the terms of its chemical fundamentals and as visualized by the flat sheet experiments, the difference between the concentration is getting smaller with increasing time. The experiment was stopped when this difference reached a value near zero as the equilibrium of the process was established.

Besides the chloride measurement also the pH value and the temperature of the feed phase were observed in order to obtain an even more comprehensive impression of the process.

5.7.3. Results

The measured concentrations during all the experiments can be found summarized in the table below.

<table>
<thead>
<tr>
<th>Time [h]</th>
<th>100 %v Aliquat ® 336 [Cl] in ppm</th>
<th>75 %v Aliquat ® 336 [Cl] in ppm</th>
<th>50 %v Aliquat ® 336 [Cl] in ppm</th>
<th>25 %v Aliquat ® 336 [Cl] in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.000 600.051</td>
<td>0.000 600.051</td>
<td>0.000 600.051</td>
<td>0.000 600.051</td>
</tr>
<tr>
<td>0</td>
<td>0.050 583.019</td>
<td>0.067 591.509</td>
<td>0.067 566.038</td>
<td>0.100 594.340</td>
</tr>
<tr>
<td>1</td>
<td>0.200 504.717</td>
<td>0.250 533.019</td>
<td>0.333 500.000</td>
<td>0.500 537.736</td>
</tr>
<tr>
<td>2</td>
<td>0.350 424.528</td>
<td>0.483 448.787</td>
<td>0.583 439.768</td>
<td>1.000 462.264</td>
</tr>
<tr>
<td>3</td>
<td>0.667 360.849</td>
<td>0.750 378.538</td>
<td>0.833 381.132</td>
<td>1.500 392.183</td>
</tr>
<tr>
<td>4</td>
<td>0.900 294.340</td>
<td>1.000 322.642</td>
<td>1.167 320.755</td>
<td>2.000 343.160</td>
</tr>
<tr>
<td>5</td>
<td>1.167 247.642</td>
<td>1.333 264.151</td>
<td>1.667 252.358</td>
<td>2.517 297.915</td>
</tr>
<tr>
<td>7</td>
<td>1.917 169.811</td>
<td>2.167 176.101</td>
<td>3.167 148.957</td>
<td>4.000 212.264</td>
</tr>
<tr>
<td>8</td>
<td>2.667 140.223</td>
<td>3.000 144.082</td>
<td>4.167 129.717</td>
<td>4.750 194.784</td>
</tr>
<tr>
<td>9</td>
<td>4.017 127.358</td>
<td>4.333 132.281</td>
<td>5.250 125.660</td>
<td>5.517 181.728</td>
</tr>
<tr>
<td>10</td>
<td>6.000 128.538</td>
<td>6.000 132.075</td>
<td>6.500 124.528</td>
<td>6.250 176.672</td>
</tr>
<tr>
<td>11</td>
<td>8.000 134.434</td>
<td>8.000 136.792</td>
<td>8.750 124.528</td>
<td>7.000 171.055</td>
</tr>
<tr>
<td>12</td>
<td>8.500 133.255</td>
<td>9.500 135.613</td>
<td>10.500 126.792</td>
<td>7.750 166.310</td>
</tr>
<tr>
<td>13</td>
<td>X X X X X X X 8.500 167.769</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As one may observe, the last few measurements fluctuate a bit and are not constantly increasing. They might derive from small temperature changes in the feed solution during the measurements but more presumable is a lack of accuracy while taking the samples. Problems with proper mixing would have a much influence than temperature. Nevertheless these errors are small and do not affect the final result massively.

Once more the correlation between a higher amount of phase transfer catalyst and a shorter period necessary for the chloride concentration to shrink down to a certain limit can be pointed out. This relation is shown in Figure 5.7.5.

Further clearly recognizable is the end of the transport process at a same concentration level what proved our expectations according to same initial conditions in all the experiments.

5.7.4. Conclusions

Due to the relatively small tube – side flow of 51 l / h, laminar flow can be supposed. According to the boundary layer theory, which defines the velocity of a flowing fluid next to the walls as zero, the resulting speed profile inside the fibers looks as shown below. But the size of the boundary layers can be assumed as really small owing to the filigree geometries of the fibers and the continuous flow of the stripping phase. This consideration enabled us again to approximate the transport mechanism without taking into account the actually hard to estimate influence of boundary layers.
Figure 5.7.6: General velocity profiles in pipes for (a) laminar flow and (b) turbulent flow

The developed transport model from the former FSSLM experiments only considers the influence of time as because of thorough mixing both the aqueous phases, the concentrations all over each particular membrane surface was supposed as equal. Already emphasized by Figure 5.7.4, the concentration of chloride is now also a function of location and shrinks constantly during flowing along a fiber what constitutes the main difference between these two techniques.

Figure 5.7.7: Flow scheme of the HFSLM experiments

Our measurements were conducted in concurrent operation, what means that stripping and feed phase flew in the same direction. Using the general equation for chemical mass balances as introduced with equation number (4) and applying it to both sub – system I and sub – system II leads to the following

26 http://me.queensu.ca/People/Sellens/images/Profiles.jpg
relations. Input and production can be set to zero once more due to no interaction of the entire system with its surrounding and no chloride generation neither in the cells nor in the membrane module.

\[ V_f \cdot \frac{d[Cl^-]}{dt} = \frac{dn_{Cl^-}}{dt} = q_f \cdot (c_{Cl_l} - c_{Cl_i}) \]

\[ V_f \cdot \frac{d[HCO_3^{-}, f]}{dt} = \frac{dn_{HCO_3^{-}, f}}{dt} = q_f \cdot (c_{HCO_3^{-}, 2} - c_{HCO_3^{-}, 1}) \]

\[ V_s \cdot \frac{d[Cl^-]}{dt} = \frac{dn_{Cl^-}}{dt} = q_s \cdot (c_{Cl_4} - c_{Cl_3}) \]

\[ V_s \cdot \frac{d[HCO_3^{-}, s]}{dt} = \frac{dn_{HCO_3^{-}, s}}{dt} = q_s \cdot (c_{HCO_3^{-}, 4} - c_{HCO_3^{-}, 3}) \]

The variable q represents the flow through the pipes and the module while the indexes 1 to 4 refer to the appropriate points shown in the flow scheme above. Up to this point already four mass balances have been obtained, albeit all of them depend on the conditions after the HF module (indexes 2 and 4) which are still unknown. To obtain these values we considered the following procedure:

![Flow Scheme](image)

Figure 5.7.8: Ion transport process in one single fiber

If the membrane is theoretically cut into lots of small parts with each a length of \( \Delta X \), the evolution shown in Figure 5.7.4 can be understood as the result of a chain reaction of lots of flat sheet membrane processes. To model this the mass balance for each sub – flat sheet module has to be evaluated. Therefore the mass balance for a differential piece of the fiber is set up

\[ Accumulation = input - output + production \]
while production can still be assumed as zero. Balancing all the substance streams for this differential membrane cell with a transfer area of

\[ A = A_{cylinder} = 2\pi \cdot r_{fiber} \cdot \Delta x \]

leads to the following relation:

\[ \frac{dn_{Cl^-}}{dt} = \pi \cdot r_{fiber}^2 \cdot \Delta x \cdot \frac{d[Cl^-]}{dt} = q_{s,1_{fiber}} \cdot [Cl^-]_x + \Delta x \cdot \pi \cdot r \cdot \Delta x - q_{s,1_{fiber}} \cdot [Cl^-]_{x+\Delta x} \]

Due to the very small diameter of the fibers the minimal difference between inner and outer radius can stay unregarded. Another appropriate approximation is the hypothesis of pseudo steady state conditions during the transport process in this differential cell. This implies that all partial derivatives with respect to time are zero. According to this the whole left part of the equation above can be kicked out. This is valid because the derivative with respect to location is much bigger than it equivalent with respect to time at “one” certain moment in the differential cell we are looking at due to almost static flow and transport conditions for very small increments of time. The simplified equation can be rewritten as

\[ q_{1_{fiber}} \cdot d[Cl^-]_x = J_x \cdot 2\pi \cdot r \cdot dx \]

and adapted to the whole membrane module by summing up all the fibers like

\[ q_{1_{fiber}} \cdot \text{number}_{fibers} \cdot d[Cl^-]_x = J_x \cdot 2\pi \cdot r \cdot \text{number}_{fibers} \cdot dx \]

The entire membrane area of the module can be calculated like this

\[ A = \text{number}_{fibers} \cdot 2\pi \cdot r \cdot l_{fiber} \]

whereas the overall flow through the fibers can be expressed as the product

\[ q = q_{1_{fiber}} \cdot \text{number}_{fibers} \]

By combining and rearranging the last three equations a differential solution for the chloride concentration evolution valid for a flow along the fiber can be obtained:

\[ \frac{d[Cl^-]}{dx} = \frac{J_x \cdot A_{module}}{\text{module} \cdot q_x} \]

The molar flux \( J \) is defined the same way as it was already introduced. According to an expecting increasing or decreasing concentration evolution the algebraic sign has to be chosen properly.
\[ J = \pm K_{\text{org}} \cdot ([\text{Aliq} - \text{Cl}]_1 - [\text{Aliq} - \text{Cl}]_2) \]

Considering this, the following system of differential equations has to be solved:

<table>
<thead>
<tr>
<th>Feed (shell – side)</th>
<th>chloride</th>
<th>[ \frac{d[\text{Cl}^-<em>f]}{dx} = -\frac{A}{L \cdot q_f} \cdot K</em>{\text{org}} \cdot ([\text{Aliq} - \text{Cl}]_1 - [\text{Aliq} - \text{Cl}]_2) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>bicarbonate</td>
<td>[ \frac{d[\text{HCO}_3^-<em>f]}{dx} = \frac{A}{L \cdot q_f} \cdot K</em>{\text{org}} \cdot ([\text{Aliq} - \text{Cl}]_1 - [\text{Aliq} - \text{Cl}]_2) ]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stripping (tube – side)</th>
<th>bicarbonate</th>
<th>[ \frac{d[\text{HCO}_3^-<em>s]}{dx} = -\frac{A}{L \cdot q_s} \cdot K</em>{\text{org}} \cdot ([\text{Aliq} - \text{Cl}]_1 - [\text{Aliq} - \text{Cl}]_2) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloride</td>
<td>[ \frac{d[\text{Cl}^-<em>s]}{dx} = \frac{A}{L \cdot q_s} \cdot K</em>{\text{org}} \cdot ([\text{Aliq} - \text{Cl}]_1 - [\text{Aliq} - \text{Cl}]_2) ]</td>
<td></td>
</tr>
</tbody>
</table>

The solution of these simultaneous equations for \( x = L \) yields the missing concentrations in point 2 and 4 as it can be seen in flow scheme Figure 5.7.7. The entire process model is obtained by solving the differential equations for the mass balances of feed and stripping beakers depending on this subordinated derivative with respect to location valid for the inner part of the membrane module.

The calculation process itself was carried out similar to the former one shown in Figure 5.6.8.: The concentration evolutions were calculated based on preset values for \( K_{\text{org}} \) which was repeatedly varied by an optimization loop in order to obtain this particular value which leads to minimal MAPE evaluating the predicted evolution compared with the measured points. The results are shown below.

Table 5.7.4.1 : Values for membrane transport constant and error according to the optimization calculation

<table>
<thead>
<tr>
<th>%v Aliquat ® 336</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{org}} ) in m/min</td>
<td>2.7375E-06</td>
<td>2.9000E-06</td>
<td>2.3250E-06</td>
<td>2.1000E-06</td>
</tr>
<tr>
<td>MAPE in %</td>
<td>9.5407</td>
<td>8.5396</td>
<td>7.2225</td>
<td>6.9335</td>
</tr>
</tbody>
</table>
Figure 5.7.9: Overview about the percentage chloride evolution for different concentrations of PTC
In comparison to the FSSLM experiments, the obtained values for the relative error of the predicted concentrations in this experiment are much higher. This mismatch is illustrated by Figure 5.7.10 to Figure 5.7.13. The calculated state of equilibrium is much lower than its experimental detected equivalent.

A further discordance with our expectations is the development of the pH value in the feed cell, which was measured continuously over the whole time the experiment was running: The initial pH value in the feed was round about 7 what reflects a neutral behavior as it is expected from a sodium bicarbonate solution. The pH value in the stripping phase was detected as approximately 9. According to a slightly
basic behavior of the bicarbonate ion also this value is reasonable and fulfilled our expectations. But with progressive time the pH value in the feed phase rose irresistibly and even exceeded the initial value measured in the feed cell by reaching 9.4 at the end of the experiment. The pH value was expected to rise according to the influx of bicarbonate, but this mechanism alone cannot explain the exceeding of the initial conditions. Due to our previous understanding of the transport process this occurrence was not possible, however a scientific foundation was found using the MEDUSA\textsuperscript{27} (Make Equilibrium Diagrams Using Sophisticated Algorithms) program issued by the Institute for Inorganic Chemistry at the Royal Institute of Technology, Stockholm.

Having implemented a large database this program creates chemical equilibrium diagrams for almost all kinds of chemical systems in variable conditions. Provided with this data we discovered that under the present conditions in the stripping phase a special species of carbonate compounds was stable which we had never seen before: $\text{NaCO}_3^-$. According to MEDUSA this ion is only produced under high concentrations of bicarbonate and not stable in low concentration environments.

27 http://quimica-analitica.ehu.es/Chemical_Diagrams/html/M_0_Main.htm
This behavior finally explains the increasing pH value in the feed cell: Due to the present equilibrium between HCO$_3^-$ and NaCO$_3^-$ under high bicarbonate concentrations

$$HCO_3^- + Na^+ \leftrightarrow NaCO_3^- + H^+$$

a movement of NaCO$_3^-$ instead of HCO$_3^-$ from the stripping to the feed phase is also possible. Caused by the lower concentration level in the feed, the stability of this ion is not provided any more whereupon it transforms back to the normal bicarbonate ion again by binding a hydrogen ion removed from the autoprotolysis equilibrium of water. The concomitant increasing concentration of the hydroxide ion OH$^-$ affects the incomprehensive rise of the measured pH value.

$$NaCO_3^- + H^+ \rightarrow HCO_3^- + Na^+$$

$$H_2O \leftrightarrow H^+ + OH^-$$

$$NaCO_3^- + H_2O \rightarrow HCO_3^- + Na^+ + OH^-$$

But the coexistence of several different species of carbon compounds in feed and stripping also have another side – effect: The interchange with chloride ions can only be done by other monovalent ions. For a low concentration level and a pH value around 7 – 8 almost all the bicarbonate is available as such a particles. In contrast, according to Figure 5.7.15, a high bicarbonate concentration level and a pH
environment near 9 provide only approximately 75% of the over – all amount of bicarbonate as univalent ions such as $\text{HCO}_3^-$ and $\text{NaCO}_3^-$. Therefore the equilibrium constant of the extraction reaction has to be adapted to these renewed conditions and readjusted. The procedure is the same as already described in chapter 2.5.4. but now with this updated equation for $K_{eq}$ due to the fact that not all the present bicarbonate is available for the extraction process. The entire amount of bicarbonate in the system is unaffected by this change and can be balanced by the help of over – all mass balances.

$$K_{eq} = \frac{([\text{Aliq} - \text{HCO}_3^-]_{\text{org}} \cdot [\text{Cl}^-]_{\text{aq}})}{([\text{Aliq} - \text{Cl}^-]_{\text{org}} \cdot 0.75 \cdot [\text{HCO}_3^-]_{\text{aq}})}$$

The recalculation of the chloride evolution in the aqueous phase can be seen below in Table 4.2.1.1 Table 5.7.4.2. The adapted value for the equilibrium constant is

$$K_{eq} = 0.28852479$$

In comparison to the former $K_{eq}$ determination the percentage error now is even smaller, what emphasizes the undertaken hypothesis about the influence of present bicarbonate concentration. Nevertheless this effect should not be taken too seriously due to the changing concentration levels during the transport process. Therefore the values mentioned before are more or less only guidelines.

<table>
<thead>
<tr>
<th>[Cl-] in [M]</th>
<th>difference [Cl-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>washing</td>
<td>measured</td>
</tr>
<tr>
<td>1</td>
<td>0.16712</td>
</tr>
<tr>
<td>2</td>
<td>0.07799</td>
</tr>
<tr>
<td>3</td>
<td>0.04258</td>
</tr>
<tr>
<td>4</td>
<td>0.02414</td>
</tr>
<tr>
<td>5</td>
<td>0.01639</td>
</tr>
<tr>
<td>6</td>
<td>0.01125</td>
</tr>
<tr>
<td>7</td>
<td>0.00649</td>
</tr>
<tr>
<td>8</td>
<td>0.00407</td>
</tr>
<tr>
<td>9</td>
<td>0.00255</td>
</tr>
<tr>
<td>10</td>
<td>0.00163</td>
</tr>
</tbody>
</table>

| MAPE | 3.3915 |

Table 5.7.4.2 : Error observation according equilibrium constant recalculation
Applying this consideration further to the following two equations, a recalculation of the hollow fiber experiment can be carried out using the same relations as before.

\[
[A_{\text{liq}} - Cl]_1 = \frac{[Cl^-]_f \cdot [A_{\text{liq}}]_{\text{ini}}}{[Cl^-]_f + K_{eq} \cdot 0.75 \cdot [HCO_3^-]_f}
\]

\[
[A_{\text{liq}} - Cl]_2 = \frac{[Cl^-]_s \cdot [A_{\text{liq}}]_{\text{ini}}}{[Cl^-]_s + K_{eq} \cdot 0.75 \cdot [HCO_3^-]_s}
\]

<table>
<thead>
<tr>
<th>%v Aliquat ® 336</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{\text{org}}) in m/min</td>
<td>2.9875E-06</td>
<td>3.1625E-06</td>
<td>2.4750E-06</td>
<td>2.2875E-06</td>
</tr>
<tr>
<td>MAPE in %</td>
<td>6.48107</td>
<td>2.05818</td>
<td>3.40151</td>
<td>2.89612</td>
</tr>
</tbody>
</table>

Table 5.7.4.3: Values for membrane transport constant and percentage error after the recalculation

A comparison with Table 5.7.4.1 points out the magnitude of the model improvement by considering this aspect. This observation is furthermore underlined by the recalculated evolution charts on the following page. The decreased amount of bicarbonate taken into account for establishing \(K_{eq}\) leads to a higher concentration level of chloride in equilibrium state.

A recalculation of the FSSLM is not necessary because of the hollow fiber experiment being the final and most interesting part of this investigation, but the result should be a better fitting as well.
The last remaining task which has to be undertaken before finishing the model is to fulfil the definition of $K_{org}$ as a real constant of membrane characteristics, since, as shown in Table 5.7.4.3, the value for the transport constant is still decreasing with an increasing amount of Aliquat ® 336 inside. To isolate a proper value for the membrane constant from the so far obtained values, a definition, which introduces the influence of changing liquid properties and environmental conditions as a specific factor, the actual constant is multiplied with, can be used:

$$K_{org, \ exp} = K_{org} \cdot f(\text{viscosity}, \text{temperature}, ...)$$
An increasing amount of Aliquat® 336 inside the membrane leads to two effects: Due to more carrier a higher transport density can be reached. This influence is considered while calculation $[\text{Aliq} – \text{Cl}]_1$ and $[\text{Aliq} – \text{Cl}]_2$ depending on the initial concentration of Aliquat® 336. Since Aliquat® 336 is a highly viscous liquid a higher concentration also correlates with a lower transport velocity. This phenomenon sophisticates the determined values for the transport constant so far wherefore its detailed influence has to be investigated.

Therefore the following viscosity measurement was conducted:

14ml Aliquat® 336 mixtures of 25, 50, 75 and 100 volume percent have been prepared three days prior to the viscosity measurements, in order to enable water contained in mixtures to form a layer. To start the measurement, a viscometer was washed by distilled water several times. Afterwards the apparatus constant was determined by measuring the time which was necessary for the water to flow out completely. After that the Aliquat® 336 solutions were put in the viscometer and the measurements were conducted similarly to the distilled water measurements.

The first step was to determine the apparatus constant for the temperature in lab. It was done using the information from the tables of viscosity and density of water and time of outflow.

The formula for dynamic viscosity is as follows

$$V = K \cdot t$$

with:

$V$ - Dynamic viscosity $\left[ \frac{m^2}{s} \right]$

$K$ – Apparatus constant $\left[ \frac{m^2}{s^2} \right]$

$t$ – time [s]

<table>
<thead>
<tr>
<th>Repetition</th>
<th>Water</th>
<th>D/K</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.75</td>
<td>58.12</td>
<td>75.87</td>
<td>108.91</td>
<td>139.43</td>
<td>242.38</td>
</tr>
<tr>
<td>2</td>
<td>23.53</td>
<td>58.13</td>
<td>74.78</td>
<td>104.31</td>
<td>145.41</td>
<td>242.28</td>
</tr>
<tr>
<td>3</td>
<td>23.50</td>
<td>59.88</td>
<td>77.12</td>
<td>108.40</td>
<td>144.06</td>
<td>244.53</td>
</tr>
<tr>
<td>4</td>
<td>23.25</td>
<td>59.18</td>
<td>74.15</td>
<td>108.71</td>
<td>149.35</td>
<td>244.00</td>
</tr>
<tr>
<td>5</td>
<td>23.41</td>
<td>58.97</td>
<td>77.13</td>
<td>107.35</td>
<td>149.75</td>
<td>243.95</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>23.69</strong></td>
<td><strong>58.86</strong></td>
<td><strong>75.81</strong></td>
<td><strong>107.54</strong></td>
<td><strong>145.60</strong></td>
<td><strong>243.43</strong></td>
</tr>
</tbody>
</table>
It was possible to estimate the K constant of the apparatus for the temperature of about 21°C.

\[ V = \frac{0.0097 \text{[m}^2/\text{s}]}{23.69 \text{[s]}} = 0.00409 \text{[m}^2/\text{s}^2] \]

Now having the K constant for the apparatus, it was possible to carry out the measurements for Decanol/Kerosene and Aliquat® 336 solutions.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>D/K</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>[g/cm³]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.791400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.797300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.801800</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.814000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.824200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass [g]</td>
<td>7.914</td>
<td>7.973</td>
<td>8.018</td>
<td>8.14</td>
<td>8.242</td>
</tr>
</tbody>
</table>

The first step for these measurements was measuring the density of each liquid. It was done by measuring the mass of a 10 ml sample. On the example of Aliquat® 336 25%:

\[ d = \frac{m}{V} \]

\( d \) – density \([g/cm³]\)

\( m \) – mass of the sample \([g]\)

\( V \) – volume of the sample \([ml]\)

The density of Aliquat® 336 25% was determined as follows:

\[ d = \frac{7.973[g]}{10[cm³]} = 0.7973 \text{[g/cm³]} \]

The next step was determining the kinematic viscosity. Knowing that

\[ V = K \cdot t \]

and having the average measured time of outflow as well as the constant K, the calculation can be done.

\[ V = 0.00409 \cdot 75.81 = 0.031043 \text{[m}^2/\text{s}] \]

Now having obtained the kinematic viscosity, it is possible to determine also the dynamic viscosity \( \mu \):

\[ \mu = V \frac{m²}{s} \cdot d \frac{kg}{m³} \]
\[
\mu = 0.031043 \cdot 797.3 = 24.751 \, [Pa \cdot s]
\]

Table 5.7.4.6: Viscosity measurements for lab temperature of about 21°C

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Water</th>
<th>D/K</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity V [m²/s]</td>
<td>0.009700</td>
<td>0.024101</td>
<td>0.031043</td>
<td>0.044035</td>
<td>0.059622</td>
<td>0.099681</td>
</tr>
<tr>
<td>Temperature</td>
<td>20.6</td>
<td>21.7</td>
<td>21.8</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

As already mentioned in the flat sheet experiment the membrane transport constant is equal to

\[
K_{org} = \frac{D}{\Delta x}
\]

with the diffusivity \( D \) as a function of the membrane specifications porosity \( \epsilon \), tortuosity \( \tau \) and membrane thickness \( e \). So the relation can be rewritten as

\[
K_{org} = f(D, \epsilon, \tau, e) = f(D, \text{constant})
\]

This means that the diffusion coefficient is the only remaining factor which is not constant for changing volume percentages of Aliquat \(^{®}\) 336 due to its accompanied change in viscosity. It is necessary to point out that not the amount of carrier but the viscosity of the membrane liquid is the important factor.

Since the diffusivity can be expressed as shown below with a still to be determined factor \( \alpha^{28} \)

\[
D = \text{constant} \cdot \frac{1}{\mu^\alpha}
\]

the experimental obtained value of \( K_{org, \text{exp}} \) is equal to

\[
K_{org, \text{exp}} = K_{org} \cdot \frac{1}{\mu^\alpha}
\]

---

The variable $K_{org}$ characterizes now a real constant which is only depending on membrane properties and the amount of carrier molecules, but not the side – effected viscosity which might be influenced by its concentration. The viscosity $\mu$ of the organic liquid inside the membrane pores is depending on both the carrier and the solvent. The value $\alpha$ is independent of specific system characteristics and will be obtained in the next steps.

Transferring the relation above into a logarithmic equation we obtain

$$\ln K_{org,\, exp} = \ln K_{org} + \ln \frac{1}{\mu^\alpha} = \ln K_{org} - \alpha \cdot \ln \mu$$

According to Table 5.7.4.3 the $\ln K_{org} - \ln \mu$ correlation should be carried out with only three pairs of variates due to a discordant value in the 50 %v measurement: An increasing amount of PTC has to lead to a lower rate of transport. Thus, the obvious too high value for $K_{org}$ should be left out while the fitting calculation in order to minimize the influence of errors.

Table 5.7.4.7 : Lookup table for the $\ln K_{org} - \ln \mu$ correlation

<table>
<thead>
<tr>
<th>$\mu$ [Pa*s]</th>
<th>$\ln \mu$</th>
<th>$K_{org}$</th>
<th>$\ln K_{org}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.47509</td>
<td>0.906278152</td>
<td>2.9875E-06</td>
<td>-12.7210736</td>
</tr>
<tr>
<td>4.85321</td>
<td>1.579640424</td>
<td>2.4750E-06</td>
<td>-12.9092702</td>
</tr>
<tr>
<td>8.21574</td>
<td>2.106051353</td>
<td>2.2875E-06</td>
<td>-12.988051</td>
</tr>
</tbody>
</table>

Figure 5.7.20 : $\ln K_{org} - \ln \mu$ correlation plot
According to this plot the relation between the experimental membrane constant and the viscosity of the membrane liquid can be evaluated as

\[
\ln K_{\text{org, exp}} = -0.225120816 \cdot \ln \mu - 12.5282156
\]

Consequently the actual membrane constant is equal to

\[
K_{\text{org}} = e^{-12.5282156} = 3.623 \times 10^{-6} \text{ [m/min]}
\]

\(\ln \mu\) was calculated on the basis of our experimental data and due to this linked to appropriate Aliquat ® 336 concentrations. In order to obtain a most generalized model, these volume percentages, referring to our prepared Aliquat ® 336 mixture at the very beginning, shall be expressed as universal volume concentrations of pure Aliquat ® 336.

Due to the fact that our initial mixture contained only 20 volume percentages of 90.4% pure Aliquat ® 336, a 100 %\text{v} membrane contains not even 0.36 M phase transfer carrier. But the maximum concentration of pure Aliquat ® 336 is almost 2 M.

\[
c = \frac{n}{V} = n \cdot \frac{\rho}{m} = \frac{\rho}{M} = \frac{880 \text{ [kg/m}^3\text{]}}{442 \text{ [kg/kmol]}} = 1.991 \text{ [M]}
\]

So this conversion is not only useful to apply our model and calculations easier to new conditions, it also helps to broaden the field of application having been limited by our experimental setup.

Table 5.7.4.8: Viscosity measurement and Aliquat ® 336 concentration conversion

<table>
<thead>
<tr>
<th>%v Aliq-mix</th>
<th>[Aliquat] M</th>
<th>%v pure Aliquat</th>
<th>(\mu) [Pa*s]</th>
<th>(\ln \mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.9073488</td>
<td>0.6457142</td>
</tr>
<tr>
<td>25</td>
<td>0.08999</td>
<td>4.52</td>
<td>2.4750934</td>
<td>0.9062782</td>
</tr>
<tr>
<td>50</td>
<td>0.17998</td>
<td>9.04</td>
<td>3.5307199</td>
<td>1.2615018</td>
</tr>
<tr>
<td>75</td>
<td>0.26997</td>
<td>13.56</td>
<td>4.8532104</td>
<td>1.5796404</td>
</tr>
<tr>
<td>100</td>
<td>0.35996</td>
<td>18.08</td>
<td>8.2157361</td>
<td>2.1060514</td>
</tr>
</tbody>
</table>
According to the plot in Figure 5.7.21 the relation between viscosity and the volume percentage of pure Aliquat ® 336 in the liquid membrane is as follows:

\[ \ln \mu = 7.95140821 \cdot 10^{-2} \cdot \% Aliq + 0.581029891 \]

Using this formula, the value of the apparently membrane constant can be connected to the volume percentage of pure Aliquat ® 336 via viscosity. The correctness of this conversion can be proved by plotting our measured point with respect to volume percentages of our prepared Aliquat ® 336 mixture against the appropriate evolution with respect to volume percentages of pure PTC. This plot represents exactly the same situation as found in Figure 5.7.16 to Figure 5.7.19.
Having implemented this last part into the MATLAB program, the experimental investigation process combined with its modeling could be seen as successfully completed.

5.8. Final conclusion

5.8.1. Achievements

Summarizing it can be said, that the hollow fiber supported liquid membrane technique is suitable to reduce the concentration of chloride ions in an aqueous phase by transferring exceeding ions to a second aqueous phase with a much smaller volume where they are concentrated in order to reduce to amount of polluted water.

The limit of chloride ions in drinking water defined by the European standard as well as by the Spanish law\(^{29}\) of 250 ppm is undershot in all the experiments without any doubts after less than four hours. With an appropriate amount of Aliquat ® 336 this period can even be shortened to less than one and a half hour. This points out the efficiency of this new procedure.

\(^{29}\) MINISTERIO DE SANIDAD Y CONSUMO. “ROYAL DECREE 140/2003 OF 7 FEBRUARY by which health criteria for the quality of water intended for human consumption are established.”
As it can be seen in Figure 5.8.2 higher initial chloride concentrations lead to earlier process stopping. This matches with our expectations due to higher levels of equilibrium state which is accompanied by faster decreasing concentration gradient inside the membrane.

As the time of the decrease of chloride is strictly dependent on the Aliquat® 336 concentration used one may expect that the best option for chloride reduction is a 100 %v solution of Aliquat ® 336. However, further investigation proved that this is not true, caused by viscosity influences.
The graph above points out a volume concentration of about 50% as most efficient. This guideline can be determined with higher accuracy by solving the following extreme value problem:

\[ J = K_{org} \cdot \left( [\text{Aliq} - \text{Cl}]_{\text{feed}} - [\text{Aliq} - \text{Cl}]_{\text{strip}} \right) \]

\[ J = K_{org} \cdot \left( \frac{[\text{Cl}_f] \cdot [\text{Aliq}_{\text{ini}}]}{[\text{Cl}_f] + K_{eq} \cdot [\text{HCO}_3^-]_f} - \frac{[\text{Cl}_s] \cdot [\text{Aliq}_{\text{ini}}]}{[\text{Cl}_s] + K_{eq} \cdot [\text{HCO}_3^-]_s} \right) \]

\[ J = K_{org} \cdot [\text{Aliq}_{\text{ini}}] \cdot \left( \frac{[\text{Cl}_f]}{[\text{Cl}_f] + K_{eq} \cdot [\text{HCO}_3^-]_f} - \frac{[\text{Cl}_s]}{[\text{Cl}_s] + K_{eq} \cdot [\text{HCO}_3^-]_s} \right) \]

The molar flux \( J \) is not only directly proportional to a faster decrease in the chloride concentration, it is its reason. Due to the fact that the viscosity influence shall be investigated the expression in brackets can be left unconsidered what simplifies to problem essentially.

\[ J \propto K_{org} \cdot [\text{Aliq}_{\text{ini}}] \]

\[ J \propto e^{-0.225120816 \cdot \mu - 12.5282156} \cdot [\text{Aliq}_{\text{ini}}] \]
After combining all the former investigated viscosity equations as seen above, the molar concentration of Aliquat® 336 in the membrane has to be expressed as a function of its volume percentage to make this problem solvable. Therefor obvious relation

\[ [\text{Aliq}_{\text{ini}}] = [\text{Aliq}_{\text{pure}}] \times \%\text{Aliq}_{\text{ini}} \]

can be used. The resulting equation is only depending on \%\text{Aliq}_{\text{ini}} , which influence can be obtained by deriving the molar flux with respect to it.

\[ J \propto e^{-1.7900274 \times 10^{-2} \times \%\text{Aliq}_{\text{ini}} - 13.836235} \times 1.99095 \times \%\text{Aliq}_{\text{ini}} \]

\[ J' \propto 1.99095 \times (e^{-1.7900274 \times 10^{-2} \times \%\text{Aliq}_{\text{ini}} - 13.836235}) \times f(\%\text{Aliq}_{\text{ini}}) \]

with

\[ f(\%\text{Aliq}_{\text{ini}}) = 1 - 1.7900274 \times 10^{-2} \times \%\text{Aliq}_{\text{ini}} \]

Due to the fact, that an exponential function cannot reach zero, only this last equation has to be assumed.

\[ J' \equiv 0 \]

\[ 0 = 1 - 1.7900274 \times 10^{-2} \times \%\text{Aliq}_{\text{ini}} \]

\[ \%\text{Aliq}_{\text{ini}} = 55.86\% \]

This means, that a concentration of around 56% of PTC inside the membrane leads to the fastest chloride transport. The second derivative does not have to be observed due to the impression given by Figure 5.8.3.

### 5.8.2. Experimental errors

According to the relatively small magnitudes of our relative errors in all the measurements, our obtained values can be used for up-scaling this procedure without any doubts. Nevertheless measured data is never unaffected by experimental errors. The following aspects can be seen as the ones with the most influence:

- Ensuring thorough mixing in feed and stripping phase
- Accuracy of sample volume taken for measurements
The time shift and concentration discordance between sampling and adding an appropriate volume of chloride mixture to replace the taken volume.

The titration method worked less accurately with a decreasing chloride concentration due to either less efficient mixing because of really high sample volumes or too small amounts of chloride ions in smaller samples.

Strictly speaking the reacting concentration percentages supplied by the MEDUSA program are changing during the process but were modeled as stable due to feasibility reasons.

An influence of the evaluation of the data can be seen in the fact that most of the calculations had to be done recursively what is attended by ongoing error propagation.

5.9. Model up – scaling

Since our lab experiment was conducted under only pseudo continuous flow conditions due to a simpler experimental set up, a small adaptation of our mathematical model has to be undertaken in order to be valid also for real continuous flows as they are required for industrial use. “Pseudo continuous” was mentioned in the sense of using beakers for containing feed and aqueous phase out of which they were flushed through the module and pumped back into their beakers afterwards. In industry the process will be carried out by flushing through certain flows only once without this particular recirculation implementation. Therefore the mass balances for both the beakers can be kicked out.

Figure 5.9.1: Considering relevant parameters for the up – scaled version

Hence the up – scaled model only contains one remaining differential equation and its derivatives are with respect to location, what is reasonable due to steady state flow conditions as they can be expected for industry. Steady state signifies that the concentration profile inside the membrane module is stabilized.
and not a function of time. These conditions are most of the times present during continuous running of the membrane system what emphasizes this approximation.

![Figure 5.9.2: Schematic concurrent (left) and countercurrent concentration profiles](image)

During our experiments we only worked in concurrent flow which was sufficient to obtain all relevant parameters. Even more common in industrial processes are countercurrent appliances though. They are characterized by higher efficiencies using equal initial conditions, well known from shell – and – tube – heat – exchangers.

By feeding the stripping phase in on the other side of the module the highest concentration of bicarbonate interacts with an already lower concentration level of chloride in the feed. This leads to two improvements compared to concurrent flow: Due to the higher amount of bicarbonate an already really low chloride concentration is still forced to decrease even further because of the presence of a strong concentration gradient. In return, also owing to the already low concentration level of chloride in the feed, the bicarbonate solution is not that much contaminated by chloride ions. As the result an only slightly polluted stripping phase is available to wash the following feed flow “fraction” further downstream.

The main advantage according to this procedure is the persistent relatively high concentration gradient all over the module as illustrated in Figure 5.9.2. This driving force of the process is shrinking down comparatively fast in the concurrent arrangement: The initial stripping phase with the highest “washing potential” interacts with the most contaminated feed conditions whereupon it gets polluted quite quickly itself. Accordingly the stripping flow loses its cleaning potential faster and both the concentration levels are matching each other after already a shorter time period.
Figure 5.9.3: Schematic efficiency comparison between concurrent and countercurrent flow, shown exemplarily by reference to an heat exchanger.

In MATLAB this was realized by implementing a preceding stripping flow concentration fitting in order to obtain the stripping concentrations at the side of the module where the feed flow is supplied, as it can be seen in Table 2.9.: Considering the changed algebraic sign of the concentration changes in the stripping flow due to the opposite flow direction, the whole system was calculated with preset stripping concentrations for \( x = 0 \). An included minimization loop then found this set of these parameters which affects to our known influx condition, underlined in grey for \( x = L \).

Afterwards the whole calculation was carried out exactly the same way as for concurrent flow, being aware of opposite algebraic signs for the feed phase evolution though.

Table 5.8.2.1: Calculation scheme for countercurrent flow

<table>
<thead>
<tr>
<th>( x )</th>
<th>( [\text{Cl}^-] )</th>
<th>( [\text{HCO}_3^-] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( [\text{Cl}^-]_0 )</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta X )</td>
<td>( [\text{Cl}^-]_0 - a )</td>
<td>( a )</td>
</tr>
<tr>
<td>( 2 \Delta X )</td>
<td>( [\text{Cl}^-]_0 - a - b )</td>
<td>( a + b )</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( L - \Delta X )</td>
<td>( [\text{Cl}^-]_0 - a - b - ... - z )</td>
<td>( a + b + ... + z )</td>
</tr>
<tr>
<td>( L )</td>
<td>( [\text{Cl}^-]_0 \cdot \Sigma (a + b + ...) )</td>
<td>( \Sigma (a + b + ...) )</td>
</tr>
</tbody>
</table>

\[ K_{eq} \]

<table>
<thead>
<tr>
<th>( \text{feed} )</th>
<th>( \text{stripping} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{Cl}^-] )</td>
<td>( [\text{HCO}_3^-] )</td>
</tr>
<tr>
<td>( (z+...+b+a) \cdot (Q_f/Q_s) )</td>
<td>( [\text{HCO}_3^-]_L \cdot (z+...+b) + a \cdot (Q_f/Q_s) )</td>
</tr>
<tr>
<td>( (z+...+b) \cdot (Q_f/Q_s) )</td>
<td>( [\text{HCO}_3^-]_L \cdot (z+...+b) + a \cdot (Q_f/Q_s) )</td>
</tr>
<tr>
<td>( ... )</td>
<td>( ... )</td>
</tr>
<tr>
<td>( z \cdot (Q_f/Q_s) )</td>
<td>( [\text{HCO}_3^-]_L \cdot z \cdot (Q_f/Q_s) )</td>
</tr>
<tr>
<td>0</td>
<td>( [\text{HCO}_3^-]_L )</td>
</tr>
</tbody>
</table>
Using this final model, provided with appropriate properties of a much bigger membrane module, the behavior of our new chloride concentration reduction technique can be calculated for any set of influx parameters. By observing its exact behavior the most efficient operating conditions were determined and theoretically up – scaled for using this procedure in the Abrera water treatment plant instead of electrodialysis.

6. Up – scaling

6.1. Preliminary considerations

Since the project’s main aim is to replace Abrera’s electrodialysis reversal process with the investigated Hollow Fiber Supported Liquid Membrane technique, the achieved results from the experiments have to be up – scaled to match the values used by the Abrera drinking water treatment plant. That means an output of 4m³ cleaned water per second has to be realized. It is not only important to check if it is possible to apply the HFSLM process in industrial scale, but also to compare its competitiveness in terms of costs, efficiency and sustainability to the common techniques used for desalination, especially electrodialysis reversal.

Currently the electrodialysis reversal technique used in the Abrera drinking water treatment plant reduces the chloride concentration to an average of 226ppm (June 2010) with an output of $4 \frac{m^3}{s}$, from which 2.3 $\frac{m^3}{s}$ is treated by electrodialysis, using 9 modules of efficiency about 0.255 $\frac{m^3}{s}$. Our main goal is to obtain at least similar efficiency, reducing chloride concentration to about 200ppm, with lower production price.

For the Abrera water treatment plant the process of chloride concentration reduction is as follows:

Figure 6.1.1: Treatment diagram including Electrodialysis Reversal Process

---

The hollow fiber supported liquid membrane technique would replace the electrodialysis reversal after an extensive pre-treatment. To achieve best possible configuration for cost efficiency the following ideas have to be taken into account:

- Optimize the number of modules, since their price is very high
- Choose the proper pumps in order to maintain desired \(4 m^3/s\) flow with the lowest power usage.
- Reduce electricity costs deriving from pumping
- Optimize sodium bicarbonate concentration in stripping flow, in order to decrease rejection percentage and minimize costs from purchase

Find the optimum rejection percentage of bicarbonate – too high percentage, directly connected with bicarbonate concentration in stripping, could decrease the number of modules required, but resupplying the bicarbonate would be extremely expensive; on the other hand, low percentage of rejection – so low initial concentration of bicarbonate – could increase number of modules.

One of our ideas was to implement to HFSLM similar flow like it is for electrodialysis in Abrera, i.e. \(2.3 m^3/s\), but reducing chloride concentration close to 0ppm. Then, \(1.7 m^3/s\) of untreated water, after mixing with the cleaned one, would lead to the present average of 228ppm.

However, using the model based on the Hollow-Fiber it was found out that to reduce chloride reduction concentration to 0 – 10 ppm an extremely high concentration of bicarbonate would be necessary. Moreover, the flow for 1 module would have to be reduced, increasing the total number of modules necessary. Overall, the costs would be significantly higher.

As it its much less expensive we decided to treat the whole flow, not only a part of it.

6.2. Model

The Model for the HFSLM technology that has been prepared based on the experimental part provides two types of flow in the module – concurrent and countercurrent. Our idea was to reach 200ppm using as little \([HCO_3^-]\) as possible, while maintaining the outflow at the level of \(4 m^3/s\).

It is important to mention that the model needs washing using bicarbonate solution. The stripping flow with bicarbonate has a minimal concentration of chloride (between 1 and 10ppm) and a proper concentration of bicarbonate, accordingly to the model obtained.

The stripping flow is equal to \(0.4 m^3/s\), derives from our final product, additionally treated with ED in order to decrease chloride concentration.
Using MATLAB modeling it was possible to estimate the optimal parameters for both types of modules, in order to decrease the costs of purchase of the membranes and minimalize the maintenance costs deriving from washing-out chloride anions using sodium bicarbonate. It was assumed that the starting chloride concentration will be around 600 mg/l, targeted to be decreased up to about 200 mg/l. The results are as follows.

### 6.2.1. Concurrent flow module

Using this operation type, stripping and feed fluxes have the same direction and are introduced both at the same side of the module. The efficiency of such modules is lower in comparison to countercurrent ones.

![Scheme of concurrent flow modules](image)

Figure 6.2.1: Scheme of concurrent flow modules

Optimal set of parameters in order to reach highest efficiency:

- Flow – $1.888 \times 10^{-4} m^3/s$
- Initial concentration of bicarbonate for washing – 0.51M
- Concentration of bicarbonate after washing, in stripping solution – 0.3977M
- Final concentration of chloride anions in treated water – 202.196ppm
- The percentage of bicarbonate to be wasted after treatment – 78.00%
6.2.2. Counter-current flow module

For this flow, the liquids have opposite flow directions.

![Counter-current flow module diagram]

Figure 6.2.2: Countercurrent flow module

Optimal set of parameters in order to reach highest efficiency:

- Flow – $1.225 \times 10^{-4} \text{m}^3/\text{s}$
- Initial concentration of bicarbonate for washing – 0.13M
- Concentration of bicarbonate after washing, in stripping solution – 0.0165M
- Final concentration of chloride anions in treated water – 197.443 ppm
- The percentage of bicarbonate to be wasted after treatment – 12.67%

Based on these values above one may observe significant differences between co-current and counter-current flows. Due to the concentration of bicarbonate used the rejected counter-current flow is much more efficient and the costs were calculated only for this one.

6.3. Cost analysis

The estimated costs for counter-current modules of HFSLM are as follows:

- Number of modules – 35556
- Purchase price – 533 333 333 €
- Sodium Bicarbonate price for 1st year – 30 610 944 €
- Supply for bicarbonate every year – 3 876 886 €
- Estimated energy costs per year – 599 184 €
- Treatment of the solution used for stripping $\frac{0.023\text{€}}{1 \text{m}^3 \text{of product}}$
• Average price for the production of 1m$^3$ of clean water using HFSLM – 0.2523 €

Formulas:

Purchase price:

\[ \text{Number of modules} \times 15000€ \]

Sodium Bicarbonate price for 1$^{\text{st}}$ year:

\[ \frac{10\% \text{ of input} \times \text{bicarbonate concentration} \times \text{mass of bicarbonate}}{90\% \text{ of input}} \times \left( \frac{m^3}{\text{year}} \right) \times \text{price} \left( \frac{0.2€}{\text{kg}} \right) \]

Supply of bicarbonate next year:

\[ \text{The percentage of bicarbonate to be wasted after treatment} \times 1\text{st year price} \]

Treatment of solution used for stripping:

\[ 0.4 \times \text{Price of electrodialysis per cubic meter} \times 0.1 \]

Estimated energy costs per year:

\[ \text{energy required} \times \text{average price of electricity} \times \text{seconds in a year} \]

Average price of production of 1m$^3$ of clean water using HFSLM:

\[ \text{bicarbonate costs} + \text{costs of treatment to prepare stripping solution} + \text{electricity costs} \]

### 6.4. Arrangement of the modules

During MATLAB modeling and the research it was found out that the way of arrangement of the modules does not influence the efficiency of the modules themselves; in other words – it does not matter whether they are connected parallel or in rows for the process. Nevertheless it has huge effect on the pumping efficiency. The modules should be put in way that enables an easy access and minimizes the area, in order to minimize possible pressure losses, what would require an increase in pump work and their number, thus the electricity cost.

During the investigations we found out that the most suitable and cost-effective arrangement is a parallel connection between all the modules.
An arrangement guarantees the lowest power usage and the lowest number of pumps needed along with a maintained flow of 4\(m^3/s\).

### 6.5. Calculating the electricity demand

Flow = \(\frac{4m^3}{s}\)

Number of modules = 35556

Pressure drop calculated from membrane datasheet \(P_2 - P_1 = 0,002\) bar

![Diagram of Water Flow Rate vs. Pressure Drop](image)

Figure 6.5.1: Pressure losses caused by one HFSLM module plotted against appropriate flows

1. Bernoulli formula

\[
\frac{\rho v^2}{2} + \rho qz + p = C
\]

2. Flow per module

\[
q_{\text{module}} = \frac{4m/s}{35556\ \text{pcs}} = 1,12 \times 10^{-4} \frac{m^3}{s}
\]

3. Density of water

\[
\rho = 1000 \ \text{kg/m}^3
\]

4. Pressure

\[
\Delta p = 0,002 \times 10^4 Pa
\]

5. Required amount of energy
\[ E = \frac{\Delta p}{\rho} = \frac{0.002 \times 10^4 \text{Pa}}{1000 \text{kg}} = 0.02 \text{J/kg} \times 1000 = 20 \text{J/m}^3 \]

6. Effect whole system

\[ E_{\text{system}} = 0.02 \frac{J}{\text{kg}} \times 35556 \text{pcs} = 711.12 \frac{J}{\text{kg}} \]

7. Effect system in Watt

\[ W = 711 \frac{J}{\text{kg}} \times 0.00028 = 0.19908 \times 1000 \text{kg} \times \frac{4 \text{m}^3}{s} = 796.32W \]

8. KW/4m³

\[ KW = \frac{769W}{1000} = 0.79KW/4m³ \]

9. Effect for Electrodialyses

\[ E = 0.6 \frac{kwh}{m³} = 600 \frac{Wh}{m³} = 600 \frac{Wh}{1000} = 0.6 \frac{Wh}{kg} \times 3600 \frac{s}{h} = 2160 \frac{Ws}{kg} = 2160 \frac{j}{kg} \]

10. Kw/4m³ for Electrodialyses

\[ W = 2160 \frac{j}{kg} \times 0.00028 = 0.6048 \times 1000 \text{kg} \times 4 \text{m}^3 = 2419.2W = 2.42KW/4m³ \]

### 6.6. Comparison with competitive techniques

While electrodialysis reversal has a relatively high demand for electricity reverse osmosis requires high pressures and has therefore a high electricity demand as well. Since HFSLM is neither electric potential gradient driven, nor pressure driven, the required energy will be less.

The overall electricity demanded by RO for efficiency equal to desired by us is 1.41 kWh per 1 m³ of treated water. It generates cost about 0.14 € for cleaning 1 m³. All of upper estimations were done using ROSA software³¹.

The overall electricity demand for electrodialysis in Abrera Water Treatment Plant³² is equal 0.6 kWh per 1 m³ of treated water. The energy cost for cleaning 1 m³ is about 0.058 €.

In case of HFSLM the energy demands is equal 0.1975 kWh per 1 m³ of treated water. The energy cost then is equal 0.0196 € for cleaning 1 m³.

---

³¹ [http://www.dowwaterandprocess.com/support_training/design_tools/rosa.htm](http://www.dowwaterandprocess.com/support_training/design_tools/rosa.htm)

The biggest disadvantage and weak point of HFSLM is the equipment price. The overall implementation costs of the modules are ten times higher than in case of ED modules installed in Abrera. Moreover, our system as well need pumps what increases equipment cost even more, but unfortunately we found no data about possible prices. Nevertheless, the price maintenance of HFSLM is relatively low, what makes our technique competitive.

Besides energy costs the following costs for maintenance have to be taken into account:

- For reverse osmosis – changing the membranes
- For electrodialysis – cleaning the membranes
- For HFSLM – sodium bicarbonate usage

The overall costs for competitive techniques are as follows:

- Electrodiaysis\(^{33}\) – 0.23 €/m\(^3\)
- Reverse Osmosis\(^{34}\) - 0.27 €/m\(^3\)
- In case of HFSLM – 0.2625 €/m\(^3\)

As one may observe, all the prices for treatment of water are similar.

Nevertheless it is worth to mention that the Electrodiaysis is cheaper than RO, especially in electricity price.

---

\(^{33}\) H.Strathmann, “Assessment of Electrodiaysis Desalination Process Costs”, Institute of Chemical Engineering, University of Stuttgart

\(^{34}\) http://www.oas.org/dsd/publications/Unit/oea59e/ch20.htm
6.7. Conclusions

According to the research done it may be concluded that the HFSLM is competitive with reverse osmosis and electorialysis. The HFSLM is suitable for chloride treatment, even though it needs additional support from one of the competitive techniques, as cost effective will be only reduction up to 200ppm. The cost of reduction to the lower concentration would be much more expensive than reduction using other techniques. That is why it is essential to use one of competitive methods in order to additionally treat water used afterwards for washing.

One of biggest advantages of HFSLM on industrial level, which is not present in other cases, is adding bicarbonate anions to the treated water, what significantly increases its quality. Not only is it less expensive than other techniques but also improve the quality of water. The example of that is the high concentration of bicarbonate in mineral water.

To sum up, the upscaled version of HFSLM is comparable than the competitive techniques. The maintenance costs are comparable with RO and ED, but as well it increases the quality of water treated, which is not present in case of another chloride treatment techniques.

7. Perspectives

During our experiments we only have investigated the functionality of the HFSLM technique for chloride concentrations from 200ppm to 600ppm, because these are the values the Abrera drinking water treatment plant has to treat. The definition of brackish water implies concentrations up to 3000 ppm, so future investigations should carry out experiments to test the efficiency of this technique for higher chloride concentrations. The higher the chloride concentration, the more bicarbonate will be replacing it, this is why the HFSLM technique might be unsuitable for seawater desalination. If the technique is applicable for higher concentrations and therefore able to treat every kind of brackish water, it would open a huge market of possible clients. India for instance has the world’s biggest lake of brackish water (Chilika Lake) and a huge demand for clean water as well. In addition to this China and Turkey have a similar situation.

Even if the HFSLM technique is not efficient for higher concentrations, it can be used in combination with other techniques as an all-in-one solution for water treatment.

The used Hollow Fiber Membranes were originally built to degas water, so the technique might be more efficient with Hollow Fiber Membranes especially designed for the purpose to desalinate water. Since the Hollow Fiber Membrane modules are one of the most important cost drivers and a large number of them is needed, developing a custom-made Hollow Fiber Membrane for desalination might enable a significant cost reduction.
During the up scaling part of the project we have figured out that our module is a bit more expensive than one of the techniques on the market (Electrodialysis), and therefore it could be done in a other way of thinking. Instead of upscale our module to clean a big amount of water it could be downscaled for just cleaning drinking water in households. According to a research made by “Vattenfall” a Swedish water production company, every person use 160L of water every day. For personal hygiene 40% of water is used, toilet visits 20%, dishing 20%, laundry 13% and only 7% for drinking water. Therefore the amount of water with low chloride concentration could be reduced significantly.

The first step would be that the big water treatment plants would only do the pre cleaning of the water that is needed. Remove only macromolecules and do disinfection. And then flow the water out to a households area where a smaller cleaning plant would be made for the drinking water. From that module it would be made pipes to every household with a freshwater output that you only connect to the kitchen. And any other water demanding facilities in the households could just operate with water directly from the water treatment plan. This could be invented to new neighborhoods where energy costs and a green thinking is important. If this would be done before the construction has taken place there would be no need for extra planning for all new pipes.

One of the ideas was implementing our technique to the yachts and ships. Unfortunately, as mentioned before, our technique is not suitable for waters of high chloride concentration. Moreover, the systems working on sea units as well provide disinfection, what is not possible in case of HFSLM. Nevertheless, our technique would be supporting such onboard system.

Another idea that could have been done to improve our project could be checking out another liquid membrane binding other ions. Not only could it have given us better view of the HFSLM but also investigation of treatment of other ions that can influence the quality of water (in case of pollution with heavy metals – Pb, Hg) could have been conducted.

Finally our project turned out to be pretty good compared with the other techniques on the market. But nevertheless half a year more work and research on different solutions, the results could be improved significantly.
8. Acknowledgements

We take this opportunity to express our deep regards to our supervisors – Teresa Coll and Agusti Fortuny for their constant guidance, monitoring and all suggestions that lead to create this document. Without their help writing this paper surely would have been much more difficult.

We also take this opportunity to express a deep sense of gratitude to Universitat Politecnica de Catalunya, for their support and seminars that have prepared us to face the challenge of doing this project.

Lastly, we would like to thank all our friends from this ERASMUS semester for supporting us and giving suggestive feedback over the entire project period.
9. Bibliography


*Amt für Veröffentlichungen*. 2011. 


CONSUMO, MINISTERIO DE SANIDAD Y. "ROYAL DECREE 140/2003 OF 7 FEBRUARY by which health criteria for the quality of water intended for human consumption are established." 2007.


http://www.guardian.co.uk/world/2008/may/14/spain.water (accessed 5 28, 2013).


*Korrosion an metallischen Werkstoffen im Trinkwasser*. n.d. 


Müller, Dr. Olaf. *Hamburger Abendblatt*. 02 21, 2011.  

*National Geographic*. n.d.  


10. Appendixes

- Alfa Aesar datasheet
- BASF datasheet
- Sodium bicarbonate characteristics, provided by Merck Chemicals
- Liqui Cell 2.5 x 8 EXTRA-FLOW PRODUCT DATA SHEET (lab scale module)
- Liqui Cell 14 x 40 EXTRA-FLOW PRODUCT DATA SHEET (industrial module used for up – scaling)
- MATLAB scripts
- CES EduPack 2012 Sustainability report for the up – scaled process version