A TALE OF TWO CHARGES:
ZWITTERIONIC POLYELECTROLYTE MULTILAYER MEMBRANES

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"Chosen examples are never serious evidence for any worthwhile generalization."

Richard Dawkins

The Selfish Gene, 1976

<i>p 9</i>	Preface
<i>p 17</i>	Introduction
<i>p 31</i>	Polyelectrolyte Multilayers For Stable Membranes
<i>p 47</i>	Polyelectrolyte Multilayers For Nanofiltration Membranes
<i>p 69</i>	Swelling Of Zwitterionic Copolymers In Aqueous Solutions
<i>p 89</i>	Zwitterionic Polyelectrolyte Multilayers For Responsive Membranes
<i>p 113</i>	Zwitterionic Polyelectrolyte Multilayers For Nanofiltration Membranes
<i>p 131</i>	Zwitterionic Polyelectrolyte Multilayers For Stable Membranes
<i>p 143</i>	Epilogue - A Tale Of Two Charges, Indeed
<i>p 153</i>	Summary/Samenvatting

P

1

2

3

4

5

6

7

8

S

Preface

"We have made some exceptional scientific advances in the last decade, and some of them -- they are not as spectacular as the man in space, or as the first Sputnik, but they are important. I have said that I thought that if we could ever competitively, at a cheap rate, get fresh water from salt water, that it would be in the long range interests of humanity which would really dwarf any other scientific accomplishment. And I am hopeful that we will intensify our efforts in that area."

John F. Kennedy

State Department Auditorium, Washington, D.C., April 12, 1961

Reaching for a refreshing glass of water on a thirsty day can be considered an obvious routine to most of the people I know. However, if we are to take the access to drinking water for granted, history can easily prove us wrong. After all, water has played a role in many conflicts. This even dates back as far as 2500 B.C., when the city of Umma (in old Mesopotamia) was deprived of water by Urlama, King of Lagash in a long lasting dispute.¹ In many more cases water has been used as a military tool. Already in primary school I was taught about the Dutch Waterline (Hollandsche Waterlinie), a series of water-based defences that could inundate the country to slow the advance of the enemy. In 1672 (the so-called “rampjaar”) the Dutch Waterline was successfully employed by William III, a turning-point in the Franco-Dutch War. More recently, the diversion of the water of the Jordan River away from Israel by Syria is said to be one of the preludes of the Six-Day War in 1967.² In 1990 claims were made by Syria and Iraq that water was used as a weapon of war when Turkey finished the construction of the Ataturk Dam, even stopping the flow of the Euphrates for a month.³ These tensions in the Middle East show that water is not only a tool to fight with, e.g., via a moat, but also a resource to fight over. Especially the latter was responsible for (or at least a factor in) conflicts in Yemen,⁴ Somalia,⁵ Kenya,⁶ Israel¹ and many more. It seems that a refreshing glass of water is maybe not that obvious.

These water conflicts show the vision of John F. Kennedy, when he made his famous statement on the need for water desalination in 1961. Often less credited in this context is an earlier American president, Dwight E. Eisenhower. Already in 1951 he declared the need for a “*farsighted program for meeting urgent water needs by converting salt water to fresh water*”. This initiated the start of the Saline Water Conversion Act a year later, which provided much needed funding of the early desalination research in the United States. This has resulted in the first synthetic membranes from Reid and Breton based on cellulose acetate that could produce fresh water from saline water.⁷ Loeb and Sourijajan used this work as an inspiration for the first asymmetric membrane that could produce fresh water with a reasonable productivity.⁸ Finally, Cadotte et al., developed a membrane based on a thin layer via an in-situ formed condensation polymer (TFC membranes),⁹ that is now the basis for almost all desalination membranes. A multitude of developments has ensured that sea water can now be desalinated at the cost of 2 kW/m³.¹⁰ This is almost an order of magnitude lower compared to the first membranes by Cadotte in 1972. I am aware this is an abstract number and unit so a comparison might be fitting: a full scale membrane desalination plant, including pretreatment, has an approximate carbon footprint of 0.92 kg CO₂eq per 1,000 liter of desalinated water, which is the about the same CO₂eq of when driving 7 miles in an average sized car.¹¹⁻¹² Although the final work of Cadotte was performed at the Filmtec Cooperation (nowadays part of the Dow Chemical Company), it was based on work carried out at the government funded Office of Saline Water Research and Development and the National Technical Information Service (NIST).⁹ This shows that for the development of such a breakthrough technology not only the brilliance of scientists is required, but also vision and commitment of governments.

Nowadays, the devotion of both scientists and politicians are again needed to tackle current and emerging water problems. Despite the fact that we are now able to make fresh water from sea water at a reasonable cost, more than a billion people still lack access to clean drinking water.¹³ Considering that we are able to desalinate water with apparent ease, I find this a shocking number and one that needs to be lowered. A major contribution to this issue is that the desalination plants (with TFC membranes from Cadotte) are often very large production plants. One of the

biggest desalination plants is, not surprisingly, located in Israel. The Ashdod seawater reverse osmosis plant (SWRO) is designed to produce 100 billion cubic meters of water per year, enough for roughly 15% of Israel's population. Such desalination plants can be considered chemical factories, requiring skilled personnel, maintenance and chemicals in order to produce water. This makes that SWRO plants are usually centralized, away from point of use. This displacement has been identified as one of the causes that today water scarcity still remains.¹⁴ Of course this is not only the case for SWRO plants, but also for other large water infrastructures such as dams. It is foreseen that the next step in water treatment follows a path that complements the existing technologies, with low cost and decentralized systems together with a collaboration between communities, companies and governments.^{13, 15} By decentralizing water treatment plants, fresh water is produced close to the point of use and access to water can be granted to more people.

My focus until now has been primarily on the desalination of seawater. I must emphasize that this focus is of a purely chronological origin and should by no means be mistaken as an origin of prominence. Closer to home we are also facing issues regarding the availability of fresh drinking water, meaning that a refreshing glass of water is at risk even in western Europe. In the Netherlands, a major part of our drinking water comes from surface water, with about 89% of the total river flow originating from outside the Dutch border.³ This is comparable to water-stressed countries such as Egypt, Sudan and Syria. Since the political situation in western Europe is stable, it is not expected that this flow will be stopped by Germany or Belgium any time soon. However, we face another issue caused by the increasing intensification of the use and reuse of fresh water resources in Europe. The contaminants that need to be removed from the water are not salts, but small organic molecules from industrial, agricultural and medicinal waste. Although these molecules do not have an acute toxicity at the current levels found in the water, prolonged exposure to them will cause long-term health effects. The reports on rising levels of emerging contaminants in our water are numerous.¹⁶⁻¹⁹ With the population growing both in number and in age, combined with an increasing welfare, newborn low molecular weight contaminants are putting a strain on good quality drinking water. A recent report on the levels of these contaminants, predominantly medicinal or endocrine disrupting components, showed not only the presence of these micropollutants in our rivers, but also that their levels are increasing downstream.¹⁹ The higher concentrations downstream the rivers, make these micropollutants a concern especially in The Netherlands. Once again, commitment from all parties involved is needed to solve this problem.

The European Water Framework Directive (EWFD) introduced at the end of the 20th century is a good initiative from the European Union to ensure the quality of surface water and groundwater throughout Europe by 2027. However, I feel that this Directive is not fulfilling its full potential and is lacking dedication. The stricter legislation on water quality that is part of the EWFD is getting severe resistance. Several European state members have raised their concerns,²⁰ and even the Dutch Water Authorities are doubtful on the new legislation.²¹ What I find striking about the opposition from especially the Dutch Water Authorities is not their inability to remove the substances from water, but the hesitation regarding the high cost that will be involved. Pharmaceutical companies have also objected against the inclusion of certain chemicals to the priority substance list, with the high costs involved as the main argument.²² All this has resulted that some chemicals that once were potential candidates for this legislation, have now not been put on the priority list of dangerous substances in water.²³ Amongst them is frequently used

medicine diclofenac, an anti-inflammatory drug, that is found to occur in our water sources²⁴ and even in Berlin tap water.²⁵

The lack of European governmental devotion to this issue is, despite the EWFD, also exposed in some of the new Horizon 2020 calls, or maybe better their absence. Although there is at the moment a call of €152,000,000 open for drinking water productions, it focusses on lowering the energy cost of desalination (NMP-24-2015 Low-energy solutions for drinking water production). One can argue if the goal set by the call, i.e. a desalination energy consumption of $<1 \text{ kW/m}^3$ is thermodynamically achievable, but maybe a better argument is the complete disregard of priority substances in this call. Other than lowering the bar, how are we to fulfill the goals of the EWFD directive by 2027 if no sufficient research is devoted on this topic? Getting and keeping fresh water available to everyone in Europe will require efforts and dedication from all parties involved, with an emphasis to low cost solutions for the removal of low molecular weight contaminants.

By now, I hope I made clear that involvement and commitment from a variety of parties is needed to ensure fresh water availability in regions of water scarcity but also in Western Europe. I also argued that this will require low-cost, preferably decentralized water treatment methods that focus on emerging contaminants. Since the work that has been carried out for this thesis has been performed at both the Membrane Science and Technology group of the University of Twente and at Pentair X-Flow, it is obvious that this thesis primarily concerns the development of such a water treatment method. The focus will be on water purification based on membranes, a concept already proven by the work of for instance Cadotte and co-workers for large scale desalination plants. Where this work deviates from that of current membrane desalination systems, is the fact that for the membrane designed here a simple operating process is always kept in mind. With this notion, low-cost and decentralized treatment methods can be technically guaranteed. In addition to this, I hope the work can be or provides a platform to address the more social and political issues at hand.

Of course I did not do all this work alone, and there are several people I would like to thank for their contribution to this thesis. First of all, I would like to thank my supervisor, professor Kitty Nijmeijer. Not only for giving me the opportunity to do my research project within her group, but also for her guidance during and her critical views on my work. Furthermore, this work would also not have been possible without professor Erik Roesink. His view on open innovation and his persuasion skills (although of the latter little was needed) is what started this project. Erik, in addition to my appreciation and respect, you now also have my sincere gratitude.

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Introduction

More and more evidence is found on rising concentrations of low molecular weight contaminants in our water and their harmful effects after prolonged exposure. These emerging contaminants, also called micropollutants, are industrial, medicinal and agricultural wastes, e.g., nonylphenol, sulfamethoxazole, atenolol and atrazine.¹⁻² They are characteristically small, with molecular weights ranging between 100 to 1,000 Dalton, and have the potential to cause long-term harm, not only to the environment, but also to human health. In order to cope with these new strains on our water infrastructure, low-cost water treatment methods, specifically designed to remove these micropollutants need to be developed. Several methods for this have been proposed, such as adsorption, oxidation or membrane filtration.³⁻⁵ As all these methods have their strengths and weaknesses, most probably a combination of different techniques will be necessary.⁶ For a low-cost treatment process, each of the individual techniques will have to be as straightforward as possible. In this thesis, we will focus on which steps can be made for membrane filtration to develop a simple process that can remove the emerging contaminants.

1.1 Hollow Fiber Nanofiltration Membranes

It is obvious that potential membranes need to have a molecular weight cut-off (MWCO) small enough to retain the different micropollutants. For instance it is known that reverse osmosis (RO) membranes can already retain many micropollutants from the water.⁷ However, even the dense RO membranes can only moderately remove some of the contaminants such as N-nitrosodimethylamine and 17 β -estradiol.⁸⁻¹¹ To cope with this, it is envisaged that even the effluent from existing RO membranes will need to be treated by an additional step in order to produce purified water.¹² The relative high operating cost of RO membranes, a combination of their higher membrane resistance and the need for an additional pre-treatment step, has led to the proposal of nanofiltration (NF) membranes as a cost-effective alternative.⁹ Numerous studies have shown that also commercially available NF membranes are capable to remove several contaminants, but that the rejection depends on both the properties of the membrane and the micropollutant.¹³⁻²¹ Although the rejections of NF membranes are significantly lower compared to RO,²²⁻²³ it is argued that this could be overcome by an appropriate post-treatment. As mentioned before, such an additional treatment would also be applied in the RO systems for a complete removal of all micropollutants. As a result, nanofiltration membranes are believed to be a more cost-effective option for the removal of micropollutants.⁹

The membrane geometry is an important aspect for low-cost membrane filtration processes, especially with regard to the fouling tendency of the membrane. All commercially available NF membranes (e.g., NF270 & NF90 from DOW, ESNA from Hydranautics, TFC-SR3 from Koch) are flat sheet membranes with a spacer in a spiral wound module. These spiral wound membrane modules have limited chemical and hydraulic cleaning possibilities and, as a consequence, are prone to (bio)fouling.²⁴ Different strategies are employed to overcome this issue as depicted in Figure 1a, typically involving an excessive pretreatment such as rapid sand filtration, coagulation and flocculation and/or ultrafiltration. The hollow fiber geometry of the ultrafiltration membranes on the other hand allows for a much higher foulant load, since clogging is less likely and these membranes can be backwashed at high pressures to remove most of the fouling. It therefore seems obvious that such hollow fiber membranes are better suited for low-cost, decentralized, processes. Since they do not need an extensive pretreatment of the feed, this results in a simplified NF process (see Figure 1). However, most of the current hollow fiber membranes are porous membranes (e.g. ultrafiltration (UF) or microfiltration (MF)) with a molecular weight cut-off (MWCO) of 10 kDa or higher, designed to remove harmful, yet mainly macroscopic sized contaminants such as bacteria, cryptosporidium and viruses. The only commercially available hollow fiber nanofiltration membranes are either Pentair X-Flows HFW1000 or some ceramic nanofiltration membranes based on TiO₂, e.g., from Inopor. The first suffers from a too high MWCO of 1,000 Da, whereas the latter is, at the moment, too expensive for a low-cost process.

Several researchers have developed hollow fiber nanofiltration membranes over the years. Often, a similar interfacial polymerization compared to the RO membranes based on thin polyamide layers is applied.²⁵⁻²⁸ Although adequate rejection properties can be obtained with such layers, the thin polyamide separation layer is not chemically stable.²⁹ These membranes thus lack cleaning possibilities with oxidants for the removal of (bio)fouling, something that is essential when no pretreatment is applied. We therefore argue that successful hollow fiber NF membranes should either be stable against hypochlorite degradation and/or have good anti-fouling properties. This means that the chemistry of the thin separation layer should be changed. For chemically

Figure 1. Flow scheme of (left) a traditional spiral wound NF process including an additional pretreatment of the feed and (right) of the proposed direct hollow fiber NF process without pretreatment.

stable NF membranes, dense layers of sulfonated poly(ether ether ketone) (SPEEK) are coated, typically on top of polyethersulfone (PES) supports.³⁰ Jung et al. applied a thin layer of SPEEK on hollow fiber UF membranes in order to remove aromatic pesticides³¹, while in a comparable way SPEEK was used by Song et al. to remove glyphosate.³² In another approach, Ji et al. cross-linked a thin polymer layer containing zwitterionic groups with glutaraldehyde on top of a porous support.³³ These membranes showed good retention, with the added benefit of a low fouling surface due to the zwitterionic groups on the surface. Although these (and many other) routes can produce fibers with good nanofiltration properties, the approaches have a major limitation: for the synthesis of these NF membranes the use of organic, often toxic, solvents and/or chemical reactions that partly degrade the support is needed.^{25, 30, 32, 34-37} We feel that an uncomplicated yet versatile technique for membrane modification, without the need for harsh chemicals, would be of great benefit for the successful development of hollow fiber NF membranes.

1.2 Polyelectrolyte Multilayer Nanofiltration Membranes

Recently, a more facile method for membrane modification based on the self-assembly of oppositely charged polyelectrolytes has received increased attention.³⁸⁻⁴⁰ In this so-called layer-by-layer (LbL) assembly, a substrate is alternatively exposed to polycations and polyanions, to build polyelectrolyte multilayers (PEMs).⁴¹ When a negatively charged substrate is exposed to a solution with an oppositely charged polycation, a charge overcompensation by the polycation flips the charge of the substrate. As a result no more polycation can adsorb. However, the obtained surface can now readily adsorb a polyanion from a solution and the process is successfully repeated, thus allowing the consecutive growth of multilayers with a controllable thickness (see Figure 2). The versatility of this approach allows the PEMs to be grown on a multitude of substrates, thus also allowing its use for the development of hollow fiber NF.⁴²⁻⁴³ For a good design of PEM membranes, it is important to understand the basic principles behind the formation of the multilayers. As this is a relatively new technique, a complete comprehension of PEMs is still lacking, and new insights are continuously obtained. Often this increase in understanding is based on PEMs on model surfaces, such as silicon wafers, and it still needs to be translated to their application in e.g., membrane filtration.

Figure 2. Schematic representation of the adsorption of polyanions and polycations using the layer-by-layer technique.

In the first publication on the LbL system in 1992, it was stated that “ionic attraction between opposite charges is the driving force for the multilayer buildup”.⁴⁴ This statement can cause the misconception that the binding enthalpy between the polyelectrolytes is responsible for the multilayer buildup. The true nature of the PEM formation was not addressed until 1999, when the counterions of the polyelectrolytes were taken into account.⁴⁵ By now, it is well accepted that the entropic gain of the release of these counterions is the main driving force in the formation of PEMs (see Figure 3). And it is this mechanism of counterion release that not only makes the formation of the PEMs possible, but also gives it its versatility and flexibility. The reason for this is that the magnitude of the entropic gain easily can be controlled by the ionic strength of the coating solutions. When more ions are already present in the solution, the entropic gain of counterions upon release is reduced. The result of this is that at higher ionic strengths, less counterions are released and thus more counterions remain bound to the polyelectrolyte. For a better clarification, Schlenoff et al. distinguished two types of charge compensation within the multilayer.⁴⁵⁻⁴⁷ When the charges of the polyelectrolyte are balanced by the oppositely charged polyelectrolyte, this is called “intrinsic charge compensation”. The other case, when the polyelectrolyte charges are balanced by counterions, is called “extrinsic charge compensation”. By changing the ionic strength during coating, the distribution between the intrinsic and extrinsic charge compensation can be steered, changing the PEM properties. In general it can be said that with increasing extrinsic charge compensation the multilayers are thicker, with a more open structure and more mobile polymer chains.^{46, 48-49} These changes in the properties of the PEM, that are so easily controlled by the ionic strength of the coating solutions, make the LbL system a promising toolbox for membrane modification.

Usually PEMs are depicted as distinct layers stacked on top of each other, kind of like a stack of Lego® bricks. Although this is probably the most comprehensible way to illustrate the layers, in reality the layers can look very different. Decher described the layers as fuzzy nanoassemblies with a significant overlap (or interdiffusion) between the different layers.⁴¹ The magnitude of the overlap between the different layers can be controlled by the coating conditions, with a higher interdiffusion when coated at higher ionic strengths.⁵⁰ The presence of an overlap between the different polyelectrolyte layers implies that multilayers have an apparent macroscopic homogeneity, quite different from a stack of distinctly different Lego® bricks. This is an important assumption, especially for dense membrane filtration applications, where solvent and solute diffuse through the whole of the layer. This means that the whole of the multilayer determines the membrane performance (unlike other applications where the performance is determined by the interfacial interactions of a multilayer and a solute). However, at both the substrate and the liquid interface this macroscopic homogeneity does not seem to be present. This can be crudely explained by the fact that near an interface, no contribution of any polyelectrolytes overlapping can come from the side of that interface. Basically, a multilayer can laterally be divided into three

Figure 3. Representation of the counterion release during the adsorption of a polycation on a surface.

regimes: a substrate dominated precursor zone (I), a bulk core zone (II) and an outer zone (III).⁵¹ Upon the layer build-up, first the precursor zone (I) grows, followed by the outer zone (III) and in the end the middle zone (II) starts growing. These transitions mean that the properties of a whole multilayer system change during the build-up of subsequent layers and that the apparent macroscopic homogeneity can only exist for multilayers consisting of numerous layers. When the exact regime a multilayer is unclear, it is wise to consider the effect of the number of layers on the performance of the multilayer system, as the properties might be a function of thickness. Especially in dense membrane filtration this is paramount when transport through the whole layer is expected.

When changing the amount of layers of PEM modified membranes, the last polyelectrolyte coated is an important parameter to incorporate in any investigation. It is known that just this so-called terminating layer can affect the properties of the full layer. The differences between a polycation and a polyanion terminated layer are the so-called odd/even effects. The most obvious odd/even effect is probably the flipping of the charge of the multilayer, e.g. from a negative poly(styrene sulfonate) (PSS) terminated layer to a positive poly(diallyldimethylammonium chloride) (PDADMAC) terminated layer. Changing the nanofiltration membrane charge by

changing the terminating layer can have a considerable effect on the rejection properties. This will especially be the case for asymmetrical salts and when the rejection is based on charge or Donnan exclusion.⁵² Besides the change in surface charge, other properties of the multilayers also show odd/even effects. For the aforementioned PSS/PDADMAC system, it is known that a PDADMAC terminated layer swells significantly more and has a higher water mobility compared to a PSS terminated layer.⁵³⁻⁵⁵ On the contrast, a PSS terminated layer has a higher surface hydrophilicity as measured by the water contact angle.⁵⁶ Recently, Schlenoff and co-workers showed that for PSS/PDADMAC multilayers, PDADMAC terminated layers are completely charge overcompensated, while for PSS terminated layers charge compensation throughout the multilayer is observed.⁵⁷ It must be mentioned that these odd/even effect are specific to the PSS/PDADMAC system, which is a PEM with high interdiffusion between the layers. This means that these effects cannot simply be transferred to other PEM systems, as they can behave quite differently. Changing only the polycation by substituting PDADMAC with poly(allylamine hydrochloride) (PAH) results in a multilayer that shows far less interdiffusion and is characterized by more distinct layers.⁴⁸

The previous comparison shows that the type of polyelectrolyte (or polyelectrolytes) significantly changes the properties of the layer. Here again, the versatility of the LbL system is reflected. This is something that can be utilized in the design of PEM membranes. Going back to the comparison of PDADMAC and PAH: not only do PSS/PAH multilayers show less interdiffusion, the higher charge density of the layers results in PEM membranes with better rejection properties both for aromatic species and for ions.⁵⁸⁻⁵⁹ Also for other polyelectrolyte pairs, Tieke and coworkers showed that the PEM becomes more dense for polyelectrolytes with a higher charge density.⁶⁰ Besides the charge density, other properties of the polyelectrolytes can be transferred to the multilayer, yielding in PEM with specific functionalities. This has for instance led to stimuli responsive,⁶¹⁻⁶⁶ sacrificial,⁶⁷⁻⁶⁹ low fouling,⁷⁰⁻⁷¹ or anti-microbial multilayers,⁷² that all can have their use in certain membrane filtration processes. Depending on the specific property of the polyelectrolyte, this can certainly be of benefit in dense filtration membranes for low cost water purification processes.

Considering that the LbL principle can be applied with a combination of basically all charged polymers, - being either strong or weak, hydrophilic or hydrophobic, linear or branched, short or long or even very long, rigid or flexible, copolymerized, stimuli responsive or low fouling polyelectrolytes - and that the properties can furthermore be tuned by the coating conditions, it seems there is plenty of work cut out for us membrane scientists.

Scope of This Thesis

The aim of this work is to understand how different polyelectrolyte multilayers can be used to make hollow fiber nanofiltration membranes. Although the basic principles behind the PEM formation are known, the modification of membranes with those layers is not always straightforward. This is especially the case when unconventional polyelectrolytes are used. The main approach through-out this thesis will therefore be combining characterization results from model surfaces with the performance of membranes modified with different PEM systems.

Since a good stability of the final membrane product is key for further product development, **Chapter 2** concerns the investigation of the long term stability of different PEM modified membranes. First the physical stability on different supports is investigated. In addition, the chemical stability of different PEM systems is explored when in contact with cleaning solutions.

In **Chapter 3**, a classical polyelectrolyte pair is used to modify an ultrafiltration membrane support under different coating conditions. The role of the ionic strength and the terminating layer on the layer and membrane properties is studied in detail.

As one of the strengths of the LbL technique is the fact that a variety of polyelectrolytes can be used, in the remaining chapters we try to utilize this by the addition of a polymer bearing zwitterionic moieties into the multilayers. First, **Chapter 4** investigates the properties of a (water) insoluble zwitterionic copolymer, investigated by means of its swelling behavior in water and different electrolyte solutions. Then a water-soluble polyzwitterion is used to build a multilayer with a polycation (**Chapter 5**) for ionic strength responsive membranes. The same polycation is also incorporated in multilayers with both a polycation and polyanion (**Chapter 6**) to yield nanofiltration membranes. In **Chapter 7**, a water-soluble zwitterionic copolymer is used to make multilayers, in order to achieve an enhanced layer stability when the membrane is exposed to high ionic strength.

In the final part (**Chapter 8**), with the obtained knowledge from the different chapters, the main scope of the thesis is revisited and future challenges of PEM modified membranes are addressed.

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Long Term Physical and Chemical Stability of Polyelectrolyte Multilayer Membranes
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Polyelectrolyte Multilayers For Stable Membranes

Abstract

This chapter presents a detailed investigation into the long term stability of polyelectrolyte multilayer (PEM) modified membranes, a key factor for the application of these membranes in water purification processes. Although PEM modified membranes have been frequently investigated, their long term stability, critical for application, has not been considered up to now. We focus on both the physical stability of the multilayer on different membranes as well as on the chemical degradation of two different multilayers in the presence of sodium hypochlorite. Two different polymeric ultrafiltration membranes are modified to become dense nanofiltration membranes by applying a thin (PEM) coating on the membrane via the layer-by-layer technique. During sequential backwash cycles, no performance loss is observed for PEM modified membranes based on sulfonated poly(ether sulfone) (SPES). On the other hand, PEM modified membranes based on the non-ionic poly(ether sulfone) (PES) show a gradual increase in permeability and loss in retention after each backwash cycle. We demonstrate that a PEM on an ultrafiltration membrane that bears ionic charges has superior adhesion to the substrate, ensuring long term stability. In addition, the chemical stability of two different multilayers is assessed by means of the resistance against sodium hypochlorite degradation. An important factor in the chemical stability is the type of polycation. Membranes coated with multilayers based on the primary polycation poly(allylamine) hydrochloride (PAH) show a loss in performance after 24,000 ppm hours NaOCl (pH 8). Membranes coated with multilayers based on the quaternary polycation poly(diallyldimethylammonium) chloride (PDADMAC) are stable for more than 100,000 ppm hours NaOCl (pH 8), which is an excellent stability, comparable to that of commercial PES ultra- and microfiltration membranes.

2.1 Introduction

A versatile method for membrane modification is the coating of membranes with different polyelectrolytes.¹ By alternately exposing the membrane to positively and negatively charged polyelectrolytes, thin polyelectrolyte multilayers (PEMs) are formed on the membrane. This so-called layer-by-layer (LbL) technique, introduced by Decher et al. in the early nineties,² offers excellent control and flexibility of the properties of these PEMs in the nanoscale range.³⁻⁴ This has led to a wide variety of possible applications of PEMs, including the modification of membranes to improve many aspects of their performance. Membranes have for instance been modified with PEMs to make membranes low fouling,⁵⁻⁶ responsive,⁷ but also to produce new nanofiltration,⁸⁻¹¹ bipolar¹², ion selective,¹³ and solvent resistant membranes.¹⁴

Until now, most of the research on PEM modified membranes has been focused on the effect on membrane performance. However, studies on the long term performance and stability of the PEM membranes under process conditions are lacking. In many filtration processes the membranes are exposed to solutes that eventually will cause fouling on the membrane. This is especially the case for aqueous applications, such as water or beverage filtration, where the process will have to cope with (bio)fouling and scaling.¹⁵⁻¹⁶ As a result, the membranes need to be cleaned periodically. Different industrially applied cleaning strategies can be utilized. Physical cleaning - by means of a backwash, a forward flush and/or air sparing - introduces high shear loads in order to remove loosely bound foulants. Chemical cleaning, e.g., pH changes or oxidation, is used to remove fouling that is bound stronger to the membrane surface. Because of the necessity of the cleaning steps, we reason that for a successful breakthrough in the application of PEM modified membranes, long term stability of the multilayers on the membrane, especially when exposed to different cleaning conditions, is paramount.

Recently, Ng et al. showed that PEM modified PES membranes have a permeability increase after a backwash of approximately 30% to 170% and noted the contribution of the lack of surface charge on the PES support towards this instability.¹⁷ These results were only for a single backwash and to our knowledge, lifetime studies that assess the long term stability of the PEMs on membranes under various cleaning conditions have not been performed. However, it is known that the polyelectrolyte complexes themselves are stable for months.¹⁸⁻¹⁹ The effect of different operation conditions on the stability of PEMs has been investigated for coated capillaries used in chromatography. Nehmé et al. showed that silica capillaries modified with poly(diallyldimethylammonium) chloride (PDADMAC)/poly(sodium 4-styrenesulfonate) (PSS) multilayer coatings, were stable over a wide pH range (2.5-9.3).²⁰ However, PEMs are known to reorder themselves under certain conditions, such as temperature, ionic strength and stress.²¹⁻²³ Especially the latter could be of influence for the long term stability of PEM membranes since high shear forces are applied during backwashing.

In addition to backwashing, membranes are often cleaned by means of an oxidative step (e.g. with sodium hypochlorite or hydrogen peroxide). The oxidative cleaning is applied to remove irreversible organic- and bio-fouling. The ability to withstand this chemical degradation (typically expressed as a product of the hypochlorite concentration and exposure time (ppm-hours)), is a major factor in determining the membrane lifetime. The stability of PEMs against such chemical treatment has been investigated only for a few occasions. Botero-Cadavid et al. investigated the degradation of poly(allylamine) hydrochloride (PAH)/poly(acrylic acid) (PAA) modified

optical sensors by H_2O_2 , and showed that over time the PEMs were degraded by the peroxide. Sato et al. showed that the degradation rate of multilayers from phenylboronic acid-bearing poly(allylamine) hydrochloride (PBA-PAH) and poly(vinyl alcohol) (PVA) was dependent on the H_2O_2 concentration. The degradation of different polycations by sodium hypochlorite was investigated by Gregurec et al.,²⁴ who showed that the stability is determined by the degree of alkylation of the amines.

In contrast, the degradation of conventional membranes by hypochlorite has been studied intensively. Both reverse osmosis (RO) and nanofiltration membranes based on polyamide thin film composites, show a significant drop in performance after prolonged exposure,²⁵⁻²⁶ mainly caused by an electrophilic attack by the hypochlorite followed by an Orton rearrangement.²⁷ Short term exposures have been shown to give small improvements in membrane performance, an effect attributed to an increase in the membrane charge density as a result of amide bond cleavage.²⁸⁻²⁹ The degradation of ultra- and microfiltration membranes based on poly(arylene sulfones) has been studied intensively as well, and their main degradation mechanism is attributed to an electrophilic attack of radicals formed by the hypochlorite.³⁰⁻³² In general it can be said that the ultra- and microfiltration membranes are more resistant against hypochlorite compared to the thin film composite RO and nanofiltration membranes. Knowledge on how the stability in hypochlorite of polyelectrolyte multilayer membranes compares to conventional membranes and how this can be influenced by the choice of polyelectrolyte is, in our opinion, key to the further development of PEM membranes and critical for the industrial application.

This is the first study that systematically investigates the long term stability of PEM modified polymeric membranes exposed to physical and chemical cleaning conditions. First, the effect of applied shear during repetitive backwashes and forward flushes on the membrane performance is investigated. For this a PEM coating, based on the well-known PDADMAC/PSS pair was applied to both a standard polyethersulfone (PES) ultrafiltration membrane and an ionically charged sulfonated polyethersulfone (SPES) ultrafiltration membrane. Both PEM modified membranes were subsequently exposed to numerous backwashes. In this way we demonstrate the important role of ionic pendant groups on the stability of a PEM on the substrate. In addition to this, the chemical stability against sodium hypochlorite oxidation of PEM modified membranes is investigated. Membranes were modified with different PEMs and exposed to sodium hypochlorite solutions. Over time, the performance of these membranes was measured. We will show that a careful selection of the polyelectrolytes is of key importance with respect to the long term chemical stability of PEM membranes.

2.2 Experimental

Chemicals

Poly(diallyldimethylammonium chloride) (PDADMAC, Mw = 150 kDa, 20 wt.% in water) was obtained from Kemira (Finland). Polystyrene sulfonic acid (PSS, Mw = 100 kDa, 20 wt.% in water) was obtained from Tosoh Organic Chemical Co., LTD (Japan). Poly(allylamine) hydrochloride (PAH, Mw = 150 kDa, 40 wt.% in water) was obtained from Nittobo Medical Co., LTD. (Japan). 15 weight% sodium hypochlorite (NaOCl) solution in water was obtained from Vivochem (The Netherlands). All other chemicals were purchased from Sigma Aldrich (The Netherlands). All chemicals were used without any further purification steps.

Membrane Materials

Polyelectrolyte multilayers were coated on hollow fibers kindly provided by Pentair X-Flow (The Netherlands). For this, two different ultrafiltration membranes were used. The UFCLE membrane is based on poly(ether sulfone) (PES), and has a molecular weight cut-off (MWCO) of 100 kDa. The HFS membrane is based on PES covered with a separation layer of sulfonated poly(ether sulfone) (SPES), and has a MWCO of 10 kDa. Both membranes are designed for inside-out filtration, having the smallest pores at the inside of the fiber. Scanning electron microscope (SEM) pictures of the membranes are made with a JEOL JSM-5600LV.

For the determination of the zeta-potential of the UFCLE and HFS membrane, single hollow fiber membranes were measured in a cylindrical cell with an electrokinetic analyzer SurPASS (Anton Paar, Graz Austria). The zeta potential is calculated by measuring the streaming current versus the pressure four times in a 5 mM KCl solution at room temperature using the following equation:

$$\zeta = \frac{dI}{dP} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \kappa_B \cdot R \quad (1)$$

where ζ is de zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution (Pa·s), ε is the dielectric constant of the electrolyte (-), ε_0 is the vacuum permittivity (F·m⁻¹), κ_B bulk electrolyte conductivity (S·m⁻¹), and R is the electrical resistance (Ω) inside the streaming channel. .

Polyelectrolyte Chemical Stability

The reactivity of hypochlorite in the presence of different polyelectrolytes was measured by means of UV-Vis. For this, 25 ml of a 0.4 g·L⁻¹ hypochlorite solution at pH 8.0 was mixed with either 25 ml of a 0.04 g·L⁻¹ polyelectrolyte solution or with 25 ml water (for the hypochlorite reference). The pH of the solutions was maintained at a pH of 8.0. Of these solutions, the UV-Vis spectra (250-500 nm) were measured every hour for 12 hours in a quartz cuvette with a Varian Cary 300 Scan UV-Vis Spectrophotometer.

Membrane Modification

For the physical stability, 100 membrane fibers were potted in 300 mm long modules, yielding a total membrane surface area of 0.063 m². PEM coatings were applied on the inside of the fibers by closing the concentrate side of the membrane module thus only allowing the coating solution to reach the inside of the fibers. Before coating, the membrane modules were wetted in

water overnight. After wetting and draining, the module was completely immersed in a $1.0 \text{ g}\cdot\text{L}^{-1}$ polycation (PDADMAC) solution with a 0.5 M NaCl concentration, with subsequent repetitive dipping every 5 minutes. After 30 minutes, the module was washed with demineralized water to remove the excess polyelectrolyte from the module. After rinsing, the module was immersed in a $1.0 \text{ g}\cdot\text{L}^{-1}$ polyanion (PSS) 0.5 M NaCl solution for 30 minutes, again with a repetitive dipping every 5 minutes. After rinsing, the membranes are coated with a single bilayer of PDADMAC/PSS. These steps are repeated in order to obtain the desired number of bilayers. For the chemical stability, single fibers were potted into a 250 mm long module. Coating of these membranes in these single fiber modules was done in the same manner as the for 300 mm modules. The coated membranes were stored in demineralized water until use for further experiments.

The coated membrane modules were characterized by means of their pure water permeability (in $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) and by means of their retention of 5 mM MgSO_4 and $200 \text{ mg}\cdot\text{L}^{-1}$ Sunset Yellow FCF. The permeability was calculated by normalizing the measured pure water flux with the trans membrane pressure. The pure water flux was measured at 20°C , with demineralized water in dead-end mode at a trans-membrane pressure of 2 bar. For the retention measurements, a tangential cross-flow through the fibers was applied. To limit the effect of concentration polarization, the cross-flow velocity of the feed through the fibers was set at $5.0 \text{ m}\cdot\text{s}^{-1}$, corresponding to a Reynolds number of approximately 3800. Salt concentrations were measured with a WTW cond 3210 conductivity meter. The concentration of the Sunset Yellow FCF dye was measured with an Varian Cary 300 Scan UV-Vis Spectrophotometer at 485 nm. The retention of both the MgSO_4 and Sunset Yellow FCF is based on the ratio between the permeate and retentate concentrations.

Polyelectrolyte Membrane Stability

The physical stability of the PEM membranes was investigated by applying multiple backwash cycles combined with a forward flush to the 300 mm modules containing 100 fibers each. During a backwash cycle, water was flown from the outside to the inside of the membrane at a pressure of 5 bar for 15 minutes. To further increase the applied shear during the backwash, a forward flush through the inside of the fibers was applied with a cross-flow velocity of $5.0 \text{ m}\cdot\text{s}^{-1}$. After each backwash cycle the membrane performance was tested, assessed by measuring the pure water permeability and the MgSO_4 retention. The presented data are an average of three different measurements.

For the chemical stability, a total of 15 single fiber modules was exposed to a 5.0 liters solution a 1,000 ppm sodium hypochlorite in water at pH 8.0. A piece of steel of $5\times 5 \text{ cm}^2$ was added to the solution in order to supply iron ions for an increased hypochlorite reactivity.³⁰ To ensure a constant hypochlorite concentration, a flow of $5.0 \text{ mL}\cdot\text{min}^{-1}$ through the membrane was applied. The hypochlorite pH was kept at pH 8.0 with HCl. The hypochlorite was refreshed twice per day, to be that sure the hypochlorite concentration did not drop below 950 ppm. Over time, the modules were taken out of the set-up and were characterized. The degradation of the membranes over time was measured again by means of the pure permeability and Sunset Yellow FCF retention.

Figure 1. SEM pictures of the two different polymeric membrane supports used in this study. Left: UFLCE membrane made from PES. Right: HFS membrane made with a separation layer based on SPES. Magnification 300x.

2.3 Results and Discussion

In the first part of the results, we will discuss the physical stability of the PEM membranes. Here we focus on the role of the polymeric membrane support that is used. In the second part, the chemical stability against oxidation with hypochlorite of different polyelectrolytes in solution and on a membrane support will be investigated.

Physical Stability

The physical stability of a PEM on a polymeric membrane support is investigated for two different membrane supports: UFCLE (PES) and HFS (separation layer based on SPES, carrying ionic pendant groups), see Figure 1. Both supports are ultrafiltration membranes with a molecular weight cut-off of 150 and 10 kDa respectively. Besides the MWCO, the main difference between the membranes is the presence of anionic groups (SO_3^-) in case of the HFS membrane. This

Figure 2. Zeta-potential at different pH values for the UFCLE and HFS membranes measured in 5 mM KCl.

difference is expressed in the zeta-potential of the membranes, shown in Figure 2. Both the UFCLE and HFS membranes are negatively charged around neutral pH, indicating that they could be used as a starting support for a polycation coating. Due to the presence of the sulfonate group on the backbone of SPES, the HFS membrane is significantly more charged. By coating both membrane types in a similar fashion, the effect on the stability of the layer of the presence or absence of these anionic groups will be investigated. For this investigation, membrane modules were alternatingly dip coated in $1.0 \text{ g}\cdot\text{L}^{-1}$ polycation and polyanion solutions with 0.5 M NaCl . For simplicity, the very common and well-studied PDADMAC/PSS based PEM was chosen.

The characterization results of the uncoated and PEM coated membranes are given in Table 1. Initially the UFCLE membrane has a higher permeability, in agreement with the higher MWCO of the membrane. Coating both supports with the same PEM of two bilayers of PDADMAC/PSS results in comparable permeabilities of both membranes, however the MgSO_4 retention of the UFCLE membrane is significantly better. An additional third bilayer on the HFS membrane yields a membrane with comparable retention as the UFCLE-(PDADMAC/PSS)₂, but with a lower permeability. This difference of the effect of the bilayers on either the open UFCLE or the more dense HFS is a clear indication that for these thin PEMs the support membrane still plays a significant role regarding the water and ion transport. The effect of the support used was also highlighted by Bruening et al.,³³ who showed significant differences between organic and inorganic supports, especially for thinner layers. In our case, due to the denser HFS support coated with two or three bilayers, the resistance to water transport is higher for the HFS coated membrane than for the open UFCLE membrane. It is expected that with more bilayers this difference between the two supports will become smaller, since for thicker PEMs the resistance of the multilayer will dominate the overall membrane transport properties. This was also seen for a PEM of 7 and more bilayers coated on either PES or alumina supports.³³

Table 1: Virgin and coated membrane properties prior to the backwash cycles.

	Permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	MgSO_4 retention (%)
UFCLE	1,100	-
HFS	80	22
UFCLE-(PDADMAC/PSS) ₂	12	84
HFS-(PDADMAC/PSS) ₂	12	52
HFS-(PDADMAC/PSS) ₃	5	78

After coating, the membranes were exposed to 6 subsequent backwash cycles of 15 min. During the backwash, water is flowed from the outside of the module towards the lumen side at a pressure of 4 bar. During this backwash, a forward flush of $5 \text{ m}\cdot\text{s}^{-1}$ was also applied at the same time. After each backwash cycle, the permeability and the MgSO_4 retention of the membranes were measured. For these experiments we used the following membranes: UFCLE-(PDADMAC/PSS)₂, HFS-(PDADMAC/PSS)₂ and HFS-(PDADMAC/PSS)₃. This allows comparison between the different supports with similar PEMs, but also different supports with comparable

Figure 3. Change in A) permeability and B) MgSO_4 retention of $(\text{PDADMAC}/\text{PSS})_n$ -coated membranes after consecutive backwash cycles. Squares: $\text{UFCLE}-(\text{PDADMAC}/\text{PSS})_2$, circles: $\text{HFS}-(\text{PDADMAC}/\text{PSS})_2$, triangles: $\text{HFS}-(\text{PDADMAC}/\text{PSS})_2$. Values are normalized for the initial values of the coated membranes.

salt retentions and permeabilities after coating. Especially the latter is relevant, as different membrane permeabilities will give different water fluxes during the backwash at 4 bar, and thus different shear forces will be applied to the membrane. In Figure 3 the permeability and MgSO_4 retention, normalized for their initial starting values, after each backwash cycle are given.

For the UFCLE coated membranes, the permeability rises after each consecutive backwash. After six backwashes, the permeability increased almost a threefold, corresponding to $35 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. The increase in permeability is accompanied by a decrease in ion rejection. After six backwashes, the rejection has more than halved from 84% to 38% MgSO_4 retention. These changes in the membrane permeability and retention are a clear indication of a change of the separation layer. PEMs are known to reorder themselves under certain conditions, such as temperature, ionic strength and stress.²¹⁻²³ Although especially the later might occur during the high shear stresses to which the layers are exposed, we feel that reordering cannot account for the considerable changes observed for our UFCLE coated membranes. This is supported by the results on the HFS coated membranes. For these membranes, no significant changes are observed in either the permeability not the retention after multiple backwashes, even though similar shear forces are applied. This stable performance of the HFS coated membranes indicates that, under the used processing conditions, no shear induced PEM reordering takes places that contributes to the significant changes in the permeability and rejection. Considering this, we reason that in the case of the UFCLE membranes, the layers are gradually removed upon backwashing. As mentioned, a major difference between the UFCLE and HFS supports is the absence of ionic charges for the former. For a good assembly of PEMs it is generally preferred to have a substrate with surface charges.³⁴ The less negative charge (as shown by the zeta-potential measurements in Figure 2) and more importantly the lack of ionic moieties of the UFCLE membrane could thus be responsible for the lower physical stability of the coated PEM observed. As the PEM will be more loosely bound to the nonionic substrate, it can be easily rinsed away when exposed to the high shear rates during the backwash combined with a forward flush.

Our results show that a PEM can be grown on both the non-ionic PES (UFLCE) and the anionic SPES (HFS) to yield denser membranes with NF like properties. However, the attachment

of the PEM onto the membrane is superior on the substrate bearing ionic charges due to the electrostatic interactions between the substrate and the multilayer. These interactions lead to an increased physical stability of the PEM membrane, which is vital for a long term use of the membrane under process conditions.

Chemical Stability

The membranes prepared in this work all have a hollow fiber geometry. Consequently the membrane feed does not require an intensive pretreatment. This in contrast to spiral wound membranes, which are prone to fouling when high loads of (organic) contaminants are used. Still, the lack of pretreatment for the hollow fiber membranes does mean that (bio)fouling on the membrane surface will occur. Although other methods are pursued to deal with (bio)fouling issues, the most common way is still chemical cleaning by means of an oxidation step. Because hypochlorite is a chemical used commonly in this oxidation step, the stability of PEM modified membranes in the presences of sodium hypochlorite over time was investigated. Based on the results of the physical stability tests, all further coating experiments were performed on the HFS support, which showed to have superior interaction with the PEM.

As the main degradation mechanism of PEM modified membranes by hypochlorite will be caused by an electrophilic attack by the hypochlorite (as is the case in polyamide and poly(arylene sulfone) membranes), (nucleophilic) polycations tend to be more susceptible towards hypochlorite degradation as polyanions. Gregurec et al. showed that for different polycations based on ammonium groups, the degree of hypochlorite degradation is dependent on the alkylation degree of the ammonium group.²⁴ Primary, secondary and tertiary polycations all have a lone electron pair and thus the possibility to donate an electron to the hypochlorite. As a result, hypochlorite reacts easily with these polycations.²⁴ In contrast, no significant changes in the UV-Vis spectra of quaternary polycations was observed.²⁴ The lack of a lone electron pair for these quaternary ammoniums gives these polycations enhanced stability against hypochlorite.

The reactivity with hypochlorite for different polyelectrolytes is illustrated in Figure 4, where the relative change in transmission at 292 nm of the solution (the absorption maximum of hypochlorite) for different mixtures is plotted as function of time. We opted here for PSS as polyanion and two well-known polycations: PAH as a primary ammonium polycation and PDADMAC as quaternary ammonium polycation. An accelerated decrease of the hypochlorite peak is a clear indication for a higher reactivity of the hypochlorite towards the polycation. Figure 4 shows a clear difference between the different polyelectrolytes. In the case of the PDADMAC/NaOCl mixture, the hypochlorite degradation rate is almost identical to that of pure NaOCl, an indication that there is hardly any reaction between PDADMAC and NaOCl. In contrast, the PAH/NaOCl mixture shows a rapid decrease in the concentration of NaOCl. Due to the oxidation of the primary ammonium groups of PAH, the NaOCl degradation rate is much higher. The mixture of PSS and NaOCl shows a slightly accelerated degradation. It is suspected that NaOCl can react with the p-electrons of the phenyl group of the PSS.

The UV-Vis results of the different polyelectrolyte/hypochlorite solutions indicate that the PEM membrane stability against hypochlorite is determined by the type of polycation. To further assess this, HFS membranes were coated with PEMs containing PSS and one of the two different polycations, PAH or PDADMAC. These different PEM modified HFS membranes

Figure 4. NaOCl degradation over time in the presence of different polyelectrolytes measured by UV-Vis at 292 nm.

were then exposed to a NaOCl solution, while measuring the evolution of the membrane retention and permeability. The conditions during the hypochlorite exposure were chosen such that hypochlorite reactivity is high: a pH of 8.0 in the presence of transition metals. It is known that there is a significant pH dependence of the hypochlorite solution on the membrane degradation.^{30,32} For poly(arylene sulfone) membranes the highest degradation rate was observed at pH 8. Furthermore, the presence of transition metals, such as iron or copper, enhances the radical formation rate via a Fenton-like mechanism.³⁰ As a result, the membrane degradation rate increases significantly in the presence of low ppm levels of the transition metal catalysts. The obtained ppm-hours of the membranes give a good indication on the difference in chemical stability of the PEMs. Since an accelerated degradation protocol is used with harsh conditions that does not mimic the actual cleaning conditions of the membrane, it must be noted that these ppm-hours will underestimate the actual expected PEM modified membrane life time. Nevertheless, the data allow the assessment of the membranes regarding their resistance against NaOCl treatment.

The results in Figure 5 show that the hypochlorite stability of the modified membranes is significantly affected by the type of polycation, which is in complete agreement with the UV-Vis results presented in Figure 4. The membranes with PDADMAC as polycation are 4 to 5 times more stable in hypochlorite compared to the membranes with PAH. In the case of the (PAH/PSS)₂ modified membranes, the membrane retention already drops after 24,000 ppm hours NaOCl. In contrast, for the (PDADMAC/PSS)₂ modified membranes only a slight drop in retention is observed at around 125,000 ppm hours. Similar difference is observed for the increase in membrane permeability. In the case of the (PAH/PSS)₂ membranes, the permeability increases rapidly, with a jump in permeability after 24,000 ppm hours. For the (PDADMAC/PSS)₂ membranes, the permeability remains relatively constant for at least 70,000 ppm hours and rises significantly after 100,000 ppm hours. It must be noted that the stability of the PDADMAC based membranes is, especially for a NF membrane, very high. Typical thin film composite membranes based on polyamides only have a tolerance of around 1,000 ppm hours.³⁵⁻³⁶ The more stable UF and MF membranes based on PES can have tolerances of 100,000 ppm hours³⁵ or even 250,000 ppm hours at pH 11.³⁷ Our results show that the PEM modified membranes, even at the harsh conditions used in this work, can have superior chlorine stability compared to commercial NF membranes and that the stability is in the range of commercial PES UF and MF membranes.

Figure 5. Evolution of retention (left) and permeability (right) in sodium hypochlorite at pH 8 of membranes coated with (PAH/PSS)₂ or (PDADMAC/PSS)₂ at 0.5 M NaCl. 1,000 ppm hours represents and exposure to 1,000 ppm NaOCl for 1 hour. The lines are added to guide the eye.

The UV-Vis results obtained for the stability of single polyelectrolytes in NaOCl are in full agreement with results of the membrane degradation with NaOCl: both demonstrate that the type of polycation is key to the chemical stability of the modified membrane. By choosing polycation that is not susceptible to electrophilic attack, in our case PDADMAC, a membrane with a very high chemical resistance is obtained. In this study only a limited amount of polyelectrolytes has been investigated and depending on the application, other polyelectrolytes might be more suited for membrane modification. Since different polyelectrolytes will yield different membrane chemical stabilities, we feel that also when other PEM systems are used it is important to investigate their stability against hypochlorite. As our work demonstrates, the simplicity of the used UV-Vis method and its good agreement with true membrane stability experiments, makes this a very useful method to quickly screen the stabilities of different polyelectrolytes.

2.4 Conclusion

For the first time, an investigation on the long term stability of polyelectrolyte multilayer (PEM) membranes is reported. The stability is determined both by the chosen membrane support and the type of polyelectrolytes. The physical stability of a multilayer on a support is significantly influenced by the presence of an ionic charge on the membrane support. Even though both SPES and PES membranes can be successfully coated with PDADMAC and PSS, only the support with ionic charges (SPES) showed high stability during subsequent backwashes.

In addition to physical cleaning, in order to remove (bio)fouling hypochlorite cleaning is often applied in industrial processes. UV-Vis measurements of polyelectrolyte solutions mixed with hypochlorite showed that the polycation PAH is very reactive with hypochlorite, whereas hardly any reactivity is observed for the polycation PDADMAC and polyanion PSS. The UV-Vis results are in agreement with the results of the long term exposure of different PEM membranes to hypochlorite. The stability of the permeability and retention of PEM modified membranes exposed to hypochlorite was a factor of 4 to 5 times higher for membranes coated with PDADMAC/PSS compared to PAH/PSS coated membranes. The UV-Vis method thus proves to be a facile way to quickly assess the polyelectrolyte stability. The high stability of the PDADMAC/PSS membranes shows that these nanofiltration membranes can withstand exposure times of

>70,000 ppm hours NaOCl at pH 8 without any significant loss in permeability and >100,000 ppm hours before any loss in retention is observed. Our results show that a careful selection of both the membrane support and the type of polyelectrolyte assures the long term stability of PEM membranes under process conditions can be assured. In addition a PEM membrane can be achieved stability comparable to that of commercially available PES based ultra- and microfiltration membranes can be achieved.

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The Role of Ionic Strength and Odd-Even Effects on the Properties of Polyelectrolyte Multilayer Nanofiltration Membranes

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Polyelectrolyte Multilayers For Nanofiltration Membranes

Abstract

The modification of membranes by polyelectrolytes via the layer-by-layer technique is an attractive method to obtain nanofiltration membranes. We prepare such membranes by alternatively coating a polycation (poly(diallyldimethylammonium chloride) (PDADAMAC)) and a polyanion (poly(styrene sulfonate) (PSS)) on a porous support. Depending on the coating conditions, hollow fiber membranes with rejections of up to 71% NaCl and 96% Na₂SO₄ are obtained. Moreover, we demonstrate that the final membrane properties can be easily controlled by variation of the ionic strength of the coating solution, the number of layers and the choice of terminating polyelectrolyte layer. Coating at higher salt concentrations results in thicker multilayers that are more open to permeation. Furthermore, we show that by taking the effect of the terminating layer (the so called “odd-even” effect) into account, information on the structure of the multilayers on the membrane is obtained. Depending on the coating conditions and number of layers, two different regimes can be distinguished. Thinner layers show a pore-dominated regime, where the multilayer is coated on the inside of the pores. Thicker layers show a layer-dominated regime, in which case the multilayer is predominately coated on top of the pores. This conclusion is supported by our ion rejection measurements: for thin layers the rejections are primarily based on size exclusion, whereas for thick layers the ion rejections are based on Donnan exclusion.

3.1 Introduction

Over the years, nanofiltration has shown to be a very versatile and powerful technique for e.g., the removal of divalent ions, the recovery of solvents and the removal of micropollutants.¹ Nanofiltration membranes can be made in a variety of different ways. Most of these methods require the use of organic solvents and/or chemical reactions that can partly degrade the support, cannot be applied on all membrane geometries and are environmentally unfriendly.²⁻⁸ A method that does not have any of these drawbacks is the layer-by-layer (LbL) approach based on water soluble polymers. The LbL technique relies on the self-assembly of polyelectrolyte multilayers (PEMs) on surfaces by alternately adsorbing oppositely charged polyelectrolytes, and gives excellent control over the properties of said surface.⁹ That is why, ever since the first publication on this topic,¹⁰ it has received increasing attention in application fields where the surface properties are essential in the overall performance.¹¹⁻¹³ Also in membrane filtration, the LbL technique is of great interest.¹⁴ The facile, often aqueous conditions and large control on layer properties make it an appealing technique to alter the membrane properties. Porous supports have for instance been coated to make forward osmosis membranes,¹⁵⁻¹⁹ low fouling membranes,²⁰⁻²³ bipolar membranes,²⁴ stimuli responsive membranes,²⁵ and monovalent selective membranes.^{22, 26} Self-standing, porous membranes from only polyelectrolytes have also been prepared.²⁷ Depending on the support and coating conditions, the PEM can be applied on the walls of a very open support or as a layer on top of a dense support.^{14, 28-30} Next to this, the thin, charged and hydrophilic PEMs are especially suited to make nanofiltration membranes. The groups of both Bruening³¹⁻³³ and Tieke³⁴⁻³⁵ were the pioneers in this field in the early 2000's. Since then, several studies on PEM nanofiltration membranes have been performed, focusing either on the application of^{21, 26, 36-39} or on the transport through the layer.⁴⁰⁻⁴³ In order to assure that the polyelectrolytes are coated as a thin film on top of the porous support, the support is typically placed in a holder and only the side with the smallest pore is exposed to the polyelectrolyte solution. However, as pointed out by Bruening, it can be difficult to assess where the PEM actually is deposited (inside the pores or on top of the support) due the lack of contrast when scanning electron microscopy imaging is used.⁴⁴ As a result, true knowledge of where the PEMs are deposited on the support is still lacking, although this information is important to understand the overall transport properties of the nanofiltration membrane.

Figure 1. Polyelectrolytes used in this study: poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS)

Studies on model surfaces, have already shown that the properties of PEMs can depend on a variety of parameters, where the ionic strength of the polymer solution used for coating is one of the most important factors.⁴⁵⁻⁵³ The ionic strength determines the charge compensation of the polyelectrolytes (PEs) in the multilayer. At low ionic strength, most of the charge compensation is between the polyanion and polycation, so-called intrinsic charge compensation. At increasing ionic strengths, charge compensation by counterions is favored, thus the equilibrium shifts to extrinsic charge compensation.⁴⁵ A change in the charge compensation from intrinsic to extrinsic is accompanied by thicker and more mobile and open layers.⁵⁴ This change will obviously affect the PEM modified membrane properties. However this can be difficult to assess, as these effects oppose each other. Thicker layers on a membrane lead to lower membrane permeabilities, whereas more open layers can increase the permeability. A systematic investigation on both the layer properties and the corresponding membrane performance will give more insight in the effect of charge compensation on the membrane properties.

In addition to the coating conditions, the properties of the total PEM are also dependent on the final layer that is adsorbed, the so-called terminating-layer. The changes with respect to the different terminating layers are often referred to as odd-even effects. By ending with either a polycation or polyanion, the surface charge⁵⁵ or the charge throughout the PEM⁵⁶⁻⁵⁷ will respectively be positive or negative. It must be noted that complete charge reversal does not always occur and this is dependent on the type of PEs, number of layers, salt concentration and the substrate.^{26, 41} In addition to the PEMs charge, odd-even effects are also shown with respect to swelling degree, water mobility and contact angle.^{47, 50, 58-59} For example, for a PDADMAC/PSS multilayer investigated by Miller and Bruening, the hydration in water for a PDADMAC terminating layer was found to be 4 times more compared to the hydration of the same system coated with an additional PSS layer.⁴⁰ These odd-even effects of the multilayer will significantly change the PEM modified membrane properties, and as such are important to take into account.

In this work, we investigate the role of salt concentration during coating on membranes modified with PEMs. For the first time, the ionic strength and the number of monolayers are systematically varied in order to examine their effect on the membrane performance. For this, we use the widely studied PE pair of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS) (see Figure 1) and coat that on tight hollow fiber UF membranes. First, we deposit the multilayers from different salt concentrations on a model silicon surface monitored in-situ by means of reflectometry.⁶⁰ This allows us to understand the growth of the multilayer systems at the different coating conditions, something that cannot be precisely monitored on the membrane itself.⁴⁴ We then use the same coating conditions to build PEMs onto a hollow fiber membrane. The membranes are characterized after each subsequent monolayer addition. We will show that by assessing the membrane properties after each monolayer, the observed odd-even effects give information on where the PEM is predominantly deposited. The approach used in this chapter provides a good insight into the properties of the PEMs on functional membranes and on how the transport properties of both water and ions through PEMs modified membranes can be controlled.

3.2 Experimental

Chemicals

Poly(diallyldimethylammonium chloride) (PDADMAC, Mw = 150 kDa, 20 w% in water) was obtained from Kemira (Finland). Polystyrene sulfonic acid (PSS, Mw = 100 kDa, 20 w% in water) was obtained from Tosoh Organic Chemical Co., LTD (Japan). All other chemicals were purchased from Sigma Aldrich (The Netherlands). All chemicals were used without any further purification steps.

Reflectometry

PEM growth on silicon wafers at different ionic strengths was measured with reflectometry. Reflectometry is a sensitive tool to study the alternating adsorption of different polyelectrolytes on flat, reflective surfaces.⁶⁰ By using a stagnation point flow cell, the measurements are done under well-defined hydrodynamic circumstances. In all cases, polyelectrolytes were exposed to the wafer until a stable adsorption plateau was obtained. We used the same procedure as describe in our previous work.²⁵ For this, 0.1 g·L⁻¹ polymer solutions with ionic strengths varying between 0.005 and 0.5 M NaCl were prepared and alternately adsorbed at room temperature on a silicon wafer with a 75 nm SiO₂ top layer. In between each polyelectrolyte adsorption an rinsing step with a background electrolyte solution was applied. For each experiment, all solutions (be it the polycation, rinse or polyanion solution) had the same ionic strength of either 0.005, 0.05 or 0.5 M NaCl. The used polymer concentration of 0.1 g·L⁻¹ provides an excess of PE per coating step, without being too high to influence the ionic strength of the solution.

In reflectometry, polarized monochromatic light (He-Ne laser, 632.8 nm) hits the wafer around the Brewster angle (71°) and is reflected towards the detector. The reflected light is split into its p- and s- polarized components. The ratio between the change in these components (ΔS) is directly proportional to the amount of mass adsorbed to the wafer, according to equation 1:

$$\Gamma = \frac{\Delta S}{S_0} Q \quad (1)$$

Where Γ is the amount of mass adsorbed on the wafer (mg·m⁻²) and S_0 is the starting output signal of the bare silicon wafer (-). Q is a sensitivity factor, which depends on the angle of incidence of the laser (θ), the refractive indices (n), the thicknesses (d) of the layers on the silicon wafer, and the refractive index increment (dn/dc) of the adsorbate. To calculate the Q -factor an optical model was used, based on the following values: $q = 71^\circ$, $n_{\text{silica}} = 1.46$, $\tilde{n}_{\text{silicon}} = (3.85, 0.02)$, $n_{\text{H}_2\text{O}} = 1.33$, $dn/dc_{\text{PDADMAC}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, $dn/dc_{\text{PSS}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, $d_{\text{silica}} = 75 \text{ nm}$.⁶¹ The sensitivity factor (Q) thus obtained to calculate the actual mass adsorption for all experiments is 26 mg·m⁻².

Membrane Modification and Characterization

PEMs were coated on hollow fibers provided by Pentair X-Flow (The Netherlands). For this, dense ultrafiltration membranes (Hollow Fibre Silica (HFS)) based on sulfonated poly(ether sulfone) (SPES) were used. The presence of the anionic SO₃⁻ group on the sulfonated polymer backbone allows for a good PEM adhesion. Untreated, these membranes have a permeability of 180 L·m⁻²·h⁻¹·bar⁻¹, an inner diameter of 0.8 mm and a molecular weight cut-off of 75 kDa. For some additional tests, denser HFS membranes were also kindly provided by Pentair X-Flow. These are hollow fibers with similar chemistry, but with a molecular weight cut-off of 10 kDa.

For PEM coating, the fibers were first completely immersed in a $0.1 \text{ g}\cdot\text{L}^{-1}$ polycation solution with the appropriate NaCl concentration (0.005, 0.05 and 0.5 M NaCl). The polyelectrolyte concentration of $0.1 \text{ g}\cdot\text{L}^{-1}$ that is used provides enough polyelectrolyte inside the membrane fiber for a layer of approximately $20 \text{ mg}\cdot\text{m}^{-2}$, an excess of polyelectrolyte, as indicated by the results from Figure 2. After 30 minutes, the fibers were subsequently rinsed in three separate NaCl solutions with identical ionic strength, after which a membrane sample was taken. The remaining samples were dipped in an alternating fashion in PSS and PDADMAC solutions in a similar way, taking a sample after each coating/rinsing step. After rinsing, all membrane samples were put in a glycerol/water (15 wt% / 85 wt%) mixture for 4 hours and then dried overnight. Single PEM coated membrane fibers were potted in a module with a fiber length of approximately 200 mm for the filtration experiments.

The water permeability (in $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) was calculated by normalizing the measured pure water flux by the trans membrane pressure. The pure water flux was measured at 20°C with demineralized water in dead-end mode at a trans-membrane pressure of 2 bar. The membrane resistance is calculated with equation 2:

$$R = \frac{\Delta P}{\mu \times J} \quad (2)$$

with the membrane resistance R in m^{-1} , J the membrane flux in $\text{m}\cdot\text{s}^{-1}$, μ the dynamic viscosity of the feed in $\text{Pa}\cdot\text{s}$ and ΔP the trans-membrane pressure in Pa . The temperature of the water during the filtration experiments was measured and kept constant at room temperature in order to avoid viscosity changes of the water.

For the salt retention measurement a cross-flow through the fibers was applied. To limit the effect of concentration polarization, the cross-flow velocity of the feed through the fibers was set at $5.0 \text{ m}\cdot\text{s}^{-1}$. This corresponds to a Reynolds number of approximately 3800, and is well in the turbulent regime. The salt concentration was measured with a WTW cond 3210 conductivity meter. The retention was based on the ratio between the permeate and concentrate concentrations.

3.3 Results and Discussion

The results presented here are divided into four major parts. First, the effect of the salt concentration on the growth of multilayers based on PDADMAC and PSS on model surfaces is investigated by means of reflectometry. In the second part, we use identical coating conditions, but now apply the layers on hollow fiber membranes. We correlate the reflectometry results and membrane permeabilities at different ionic strengths, in order to assess the role of the ionic strength during coating on the (layer) properties on the membrane. In the third part, we take the odd-even effect into account to understand how the terminating layer further determines the membrane properties. In the final part, we investigate the salt rejection of the membranes coated at different ionic strengths. Based on the result from the first three parts, we will identify different ion rejection mechanisms resulting from the different coating conditions.

Figure 2. A) Multilayer growth monitored as measured with reflectometry, showing the subsequent adsorption of PDADMAC (+) and PSS (-) at $0.1 \text{ g}\cdot\text{L}^{-1}$ in 0.05 M NaCl . Flushing with a background electrolyte solution (0.05 M NaCl) is indicated with "s". B) Effect of NaCl concentration for (PDADMAC/PSS)_n on the multilayer plateau thickness as obtained with reflectometry.

Multilayer Growth on Silicon Wafers

With reflectometry, the amount of mass adsorbed onto a silicon wafer is measured over time. A typical multilayer growth on a silicon wafer, as measured with reflectometry, is presented in Figure 2. By alternating between the deposition of PDADMAC (+) and PSS (-), a multilayer is formed on the surface. Prior to flowing a polymer solution through the cell, the cell is always rinsed with a background electrolyte solution with identical ionic strength (s). This prevents the formation of complexes of PDADMAC and PSS in the bulk. It is known that the layer buildup, especially at higher salt concentrations can be influenced by shear forces applied to the polyelectrolyte.⁴⁹ By using the stagnation point flow cell, the polyelectrolyte is deposited under well-defined hydrodynamic circumstances, without any applied shear. At the measuring spot on the wafer the solution is stagnant, meaning that polyelectrolyte transport is purely diffusion based and that the electrostatic interactions between the substrate and the polyelectrolyte solution determine the layers properties. Figure 2a shows that, under these hydrodynamic conditions, each subsequent depositing step is stabilized within minutes, reaching a plateau value.

The ionic strength of the polyelectrolyte solutions is an important parameter to control the multilayer growth and its properties.^{45, 54} The effect of the ionic strength on the layer growth is shown in Figure 2b. At low ionic strength, the charge compensation of the polyelectrolytes is dominated by electrostatic interactions between the polymer chains, the so-called intrinsic charge compensation. This results in thin and dense multilayers with a relatively low mobility of the polymer chains. Upon increasing the ionic strength during the layer growth, more of the ionic charges of the polyelectrolytes are screened by the free ions from the solutions, resulting in more extrinsic charge compensation. The extrinsic charge compensation is accompanied by thicker and more open (hydrated) multilayers with higher polymer chain mobility.⁵⁴ The results in Figure 2b show the effect of the transition from intrinsic to extrinsic charge compensation. At higher ionic strengths more polyelectrolyte is adsorbed on the silica surface. In the case of 0.5 M NaCl , a non-linear layer growth is observed instead of a linear growth (0.005 and 0.05 M NaCl). This non-linear growth is typical for PDADMAC/PSS multilayers at higher concentrations and has an onset at around 0.3 M NaCl .⁴⁶ The more open structure of the multilayers at higher ionic strength allows for substantial polyelectrolyte "in" diffusion in the layer, leading to thicker

Figure 3. Effect of NaCl concentration on $(PDADMAC/PSS)_n$ on the membrane resistance. All data are for a PE concentration of $0.1 \text{ g}\cdot\text{L}^{-1}$, at NaCl concentrations of 0.005 M (■), 0.05 M (●) and 0.5 M (▲).

layers. This non-linear growth is also observed for other PE combinations, which typically show weaker interactions.^{46, 56, 62-65} The results show a significant role of the ionic strength on the layer properties, and we can use this to control the properties of PEM modified nanofiltration membranes.

Membrane Modification

Via dip coating, negatively charged HFS membranes are coated with PDADMAC/PSS multilayers. The coating conditions used were the same as used on the silicon wafer. By dip coating the membranes, transport of the polymer to the membrane is mainly based on diffusion within the fiber. As we immerse the fiber completely in the coating solution, PE deposition is not limited to the inner surface of the membrane only and the whole porous structure can be coated by the PEs. The effect of coating the HFS membranes at different ionic strengths on the membrane resistance is shown in Figure 3. The observed zig-zag behavior is a clear indication that odd-even effects influence the membrane resistance, something that will be discussed in detail in later in this chapter. In this section, we will focus on the effect of the ionic strength and the number of layers on the membrane properties.

For all NaCl concentrations, the membrane resistance increases with the number of bilayers. A significant effect of the ionic strength on the membrane resistance is observed. With increasing ionic strength of the coating solution, the membrane resistance per bilayer increases substantially. This is completely in line with the results from the multilayer growth as measured with reflectometry (Figure 2b). At higher ionic strengths, thicker layers are formed on the membrane due to increased extrinsic charge compensation within the multilayers. These thicker layers results in an increased pore size decline and/or thicker PEM on the membrane surface and as such a higher membrane resistance.

For solution diffusion based membrane processes, the membrane resistance to water permeation is determined by three factors⁶⁶: the solubility, the diffusivity and the layer thickness. Regarding the latter, increasing the layer mass will increase the layer thickness and will be a direct result of the amount of coating steps, but this will also depend on the salt concentration.⁴⁵ The results from Figure 3 indicate that per coated bilayers, the amount of polymer adsorbed dominates the

membrane resistance. At 0.5 M NaCl, where significantly more PE is adsorbed, a severe increase in the membrane resistance is obtained, whilst the layers obtained from 0.005 M NaCl show little increase in the membrane resistance. To better understand the multilayer properties it is important to address, in addition to the thickness, the solubility and diffusivity as well.

For dense membranes, in e.g. gas separation, the solubility and diffusivity are mainly determined by the (excess) free volume of the polymer layer and the affinity of the solute to the layer. In the case of the multilayers for water filtration, we reason that the hydration of the layer is a better way to describe the solubility and diffusivity in these films. The hydration is a term that is commonly used to describe the properties of the LbL films.⁶⁷ An increase in hydration leads to more open, swollen, layers with more volume between the polymer chains. For the multilayers, the hydration can be controlled by changing the salt concentration during coating.^{45,54} In Table 1 we investigate if the membrane resistance to water permeation is solely determined by the layer mass or whether the hydration of the layer also plays a role.

Table 1: Comparison of PEM mass and membrane permeability for layers coated from different [NaCl]

Layer type	Layer mass [mg·m ⁻²]	Water permeability [L·m ⁻² ·h ⁻¹ ·bar ⁻¹]
(PDADMAC/PSS) ₆ -PDADMAC from 0.05 M NaCl	8.9	16.7
(PDADMAC/PSS) ₂ -PDADMAC from 0.5 M NaCl	8.6	34.9
(PDADMAC/PSS) ₄ -PDADMAC from 0.5 M NaCl	35	16.2
(PDADMAC/PSS) ₅ from 0.05 M NaCl	5.7	27.5
(PDADMAC/PSS) ₂ from 0.5 M NaCl	5.8	81.7
(PDADMAC/PSS) ₃ from 0.5 M NaCl	13	47.5

In Table 1 the membrane permeability (the pressure normalized flux, a more comprehensible number compared to the membrane resistance) is compared in relation to the measured adsorbed amounts on a silicon wafer. Here we have chosen to compare a membrane prepared at 0.05 M NaCl, to two membranes coated at 0.5 M NaCl, one with the same layer mass, and one with the same permeability but a different layer mass. This allows us to disregard the layer mass, and to observe differences in the solubility and diffusivity (which are function of the hydration) of the layers. In order to rule out any odd-even effects of the multilayers, we only compare layers with the same terminating PE. Although, the substrates in the two systems are different, we think that the data from the reflectometry provide a good indication of the layer mass on the membrane as well. An additional comparison is provided in the Appendix Chapter 3 (Figure 9). Table 1 shows that similar layer masses have substantially lower permeabilities when coated from 0.05 M NaCl as compared to 0.5 M NaCl. The lower permeability at a similar mass thus means that the solubility and diffusivity are lower at decreased ionic strength during the coating, resulting in a denser membrane. This denser layer at 0.05 M NaCl fits well with the expected increasing contribution of intrinsic charge compensation in the multilayer, which leads to lower multilayer hydration.⁴⁵ As a result of this, a significant increase in PE layer mass is needed in the case of 0.5

M NaCl to obtain comparable permeabilities to the membranes coated at 0.05 M NaCl. For PSS terminating layers, this means that more than twice the layer mass still results in higher permeabilities when coated from 0.5 M NaCl as compared to 0.05 M NaCl. Table 1 also shows that by comparing 6.5 bilayers from 0.05 M compared with 4.5 bilayers from 0.5 M NaCl, around 4 times the layer mass is needed to obtain comparable permeabilities.

The results shown here highlight the importance of the coating conditions on the design of PEM modified membranes. Since both the amount of layers and the ionic strength during coating affect the membrane permeability, it is essential that both parameters are regarded in optimizing and controlling the PEM modified membrane properties.

Odd-Even Effects on Membrane Permeability

For two given polyelectrolytes, the terminating layer in PEMs determines, next to the salt concentration during coating, most of the total layer properties. In addition to the obvious changes in the surface properties, such as contact angle and surface charge, the bulk properties of the film also show distinct changes dependent on the terminating layer and these are collectively called odd-even effects.^{38, 40, 47-48, 57-59} As in the PEM modification of our fibers we always switch between a final coating of the polycation to a final coating of the polyanion and back, it is important to take these odd-even effects into consideration.

In Figure 3 we already pointed out a distinct zig-zag effect, indicative of odd-even effects on the membrane performance. In Figure 4 we show these effects even more clearly, by comparing the permeability of the membranes coated from either 0.005 or 0.5 M NaCl for 7 monolayers and onwards. In both cases, there is a clear odd-even effect observed for the membrane permeability. In the case of 0.005 M NaCl, the membrane permeability increases when an additional PSS layer is coated and decreases again when a PDADMAC layer is applied. However, in the case of 0.5 M NaCl, the trend is vice-versa, showing a decrease in permeability when an additional PSS layer is applied and an increase after PDADMAC. This inverse behavior of the odd-even effect is only observed for multilayers consisting of 7 monolayers or more when coated from 0.5 M NaCl. Initially, for layers coated from 0.5 M NaCl a similar odd-even effect as compared to the 0.005 M NaCl layers is shown. After the sixth monolayer, the odd-even effect shows a flip that results in the inverse behavior shown in Figure 4. This flip can clearly be observed in Figure 3. Also for the layers coated at 0.05 M NaCl initially higher permeabilities are observed for PSS terminating

Figure 4. Odd-even effects on the permeability of membranes coated with $(\text{PDADMAC}/\text{PSS})_{3.5+n}$ layers at 0.005 M NaCl (●) and 0.5 M NaCl (■).

layers. However, after 12 monolayers the odd-even effects seems to disappear in case of 0.05 M. This can indicate a transition of the odd-even effect. This flipping and the subsequent striking difference in the odd-even effect can give, as we will show, information on the dominating mechanism in the water transport through the membrane.

To understand these effects, it is key to discuss odd-even effects in more detail. Membrane hydrophilicity plays an important role on the water transport resistance as more hydrophilic membranes tend to have higher permeabilities. It was shown that the contact angle of PDADMAC/PSS multilayers is dependent on the terminating layer, with the more hydrophobic PDADMAC resulting in around 10-30° higher contact angles.^{37-38, 50} The increase in hydrophilicity for PSS terminating layers can thus cause an increase in the membrane permeability with an additional layer (as shown with 0.005 M NaCl). However, this is expected to be the case for all instances, and cannot explain the flipping of the odd-even effect shown here. Similar reasoning can be employed with regard to the water mobility in the PEM. McCormick et al. showed that the water mobility is higher in the case of PDADMAC terminating layers.⁵⁹ This can explain the increase in membrane permeability when an additional PDADMAC is coated on the fiber (in the case of 0.5 M NaCl). As this change in water mobility is also expected to occur in all instances, again the flipping of the odd-even effect cannot be explained based on water mobility alone.

The swelling degree of PDADMAC/PSS PEMs also changes based on the terminating layer, with a PDADMAC terminating layer showing a higher swelling degree of up to a 4 fold more.^{40-41, 58, 68} For PDADMAC terminated layers water mobility has also shown to be increased. The swelling degree of polymer films can change the membrane permeability. An increase in swelling leads to thicker but less dense polymer layers. As a result, the permeability through the layer will be increased. The keyword here is “through”: when the major resistance of the water transport is indeed through the PEM, an increase in swelling will result in an increase in the membrane permeability.^{25, 69} Su et al. indeed showed that the higher swelling degree of PDADMAC terminating layers causes a higher membrane permeability.³⁸ However, when the major resistance of the water transport is not through the film, but through the smallest pores of the membrane, the result can be quite the opposite. When the pores of the membrane are coated with the PEM, an increase in swelling of that multilayer will result in a pore size decline and subsequently a reduced membrane permeability.⁷⁰ This is an opposite response to the case where the majority of the resistance is through a multilayer, and thus can explain the observed flipping of the odd-even effect. The effect is schematically represented in Figure 5, where we present two cases. Case 1, the pore-dominated regime, applies for thinner films, where the major resistance is in the transport through the coated pores. For Case 2, the layer-dominated regime, the multilayer is much thicker, and the insides of the small pores can no longer be coated and a PEM film is formed on top of the pore.³⁰ As a result, the major resistance for thick PEM films will be through the multilayer. For the pore-dominated regime, an increase in PEM swelling reduces the permeability, whereas for the layer-dominated regime an increase in PEM swelling increases the permeability. This explains the different odd-even effects that we observe and also explains the observed flip. When the multilayer becomes thicker and thicker, there will be a transition from the pore dominated regime to the layer dominated regime, leading to a flip from one odd-even effect to another. The relative quick flipping of the odd-even effect within just 3 monolayers for 0.5 M NaCl can be explained by the fact that at the same time the growth rate of the PEM significantly increases at 5 to 7 monolayers. This is shown by the non-linear growth in Figure 2.

Figure 5. A schematic representation of the two different cases that determine the membrane resistance.

TOP: Case 1, the pore-dominated regime: the higher swelling degree (SD) of PDADMAC terminating layers results in smaller pores, increasing the membrane resistance compared to PSS terminating layers.

BOTTOM: Case 2, the layer-dominated regime: for thicker layers, the smaller pores can no longer be coated and the PEM that grows on top of the pores dominates the resistance. The higher SD of a PDADMAC terminating layer results in more open layer with a lower resistance compared to the PSS terminating layer.

This change in location of the dominating resistance is, next to the swelling degree, also in agreement with the odd-even effects of the contact angle and water mobility. In the case of the resistance through the pores, the pore hydrophilicity will significantly affect the water transport. Pores coated with a PSS terminated PEM are more hydrophilic and thus show a higher permeability. In the case of the major resistance being through the film, the transport of the water through the bulk PEM becomes important. As such PSS terminating layers exhibiting a lower water mobility, will have a lower permeability.

To confirm the above conclusion of the transition of pore-dominated odd-even effect to a layer-dominated odd-even effect, we performed the same experiments with denser membranes with a MWCO of 10 kDa (see Appendix Chapter 3). Our results with these denser membranes support our findings. Here we only applied the coating solution on the inside of the fiber, thus predominantly coating in the inner surface of the membrane. For these membranes, the PDADMAC terminating layer showed higher permeabilities as the subsequent PSS layer, without a flipping of the odd-even effect (see the Appendix Chapter 3). For these dense membranes, as one would expect, we were thus in the layer dominated regime already from the first layer of adsorbed polyelectrolyte.

Salt Rejection of PEM Modified Membranes

In previous sections it was clearly shown that both different coating conditions and the terminating layer affect the water transport of the membrane. In the same line of reasoning, it is also of interest to investigate how the rejection of ions is affected. For this, we investigated the ion

rejection of membranes coated at 0.005 M, 0.05 M and 0.5 M NaCl. To get insight in the role of the terminating layer, for each coating condition we compared retentions of membranes coated with (PDADMAC/PSS)₆-PDADMAC and (PDADMAC/PSS)₇. The rejections are measured for three different ion pairs, namely NaCl, CaCl₂ and Na₂SO₄, all at a concentration of 5 mM. The results are shown in Figure 6.

The retention of ions can be based on (a combination of) several mechanisms. In dense membranes, the solution-diffusion model alone can properly describe the ion rejections.⁴² However, in the case of more open nanofiltration membranes, convective transport through pores can also influence the rejection.⁴² Furthermore, if the nanofiltration membrane is charged, Donnan exclusion should be taken into account.⁷¹ Since the resistance of our membranes is either pore-dominated (in the case of thin layers) or layer-dominated (in the case of thicker layers), it is expected that these distinctions will also affect the rejection mechanism.

For the thin layers obtained at 0.005 M NaCl, little rejection for all ions is observed due to the relatively larger pore size of the membrane. For ions dissolved, the dynamic hydrated radius is a good indication of the size of the ions in water. Even though the size differences are not large, the order of the different ions used here is: $\text{Na}^+ < \text{Cl}^- < \text{Ca}^{2+} < \text{SO}_4^{2-}$.⁷² For both membranes, the highest retention is obtained for the ion pair with the large SO_4^{2-} . Only small differences are observed between the PDADMAC and PSS terminating layers, showing that the charge of the membrane does not play a significant role here. For these membranes, both membrane charge and solution diffusion only play a minor role in the rejection, and size exclusion via convective transport dominates. This indication of size exclusion is in full agreement with our previous results, where we concluded that for thin layers the transport is pore-dominated.

The results from membranes coated at 0.05 and 0.5 M NaCl show that for membranes coated with thicker PEM layers, the ion radii have little effect on the retentions properties. This is in agreement with our previous results that indicate a layer-dominated regime for membranes coated with thicker PEMs. For membranes coated at 0.05 M NaCl, the retention is dependent on the type of ion and on the terminating layer. The positive PDADMAC terminated membrane has the highest retention for the bivalent cation Ca^{2+} and lowest retention for SO_4^{2-} . The negative

Figure 6. Retentions of 5 mM CaCl₂, NaCl and Na₂SO₄ of membranes coated with (PDADMAC/PSS)₆-PDADMAC and (PDADMAC/PSS)₇ at either 0.005, 0.05 and 0.5 M NaCl. Retention measurements were performed in crossflow mode with a Reynolds number of approximately 3800.

PSS terminated membrane shows the opposite trend. This is in accordance with the Donnan exclusion model, typical for charged nanofiltration membranes.⁷¹ When comparing only the NaCl retention, the PSS terminated membrane shows a significantly higher retention than its positive counterpart. This is explained by the lower swelling degree of the PSS terminating layer, which results in denser layers compared to the PDADMAC terminating layer. Again an indication that the ions pass through the layer, and thus that the layer dominated regime is prevalent.

The PDADMAC terminated membranes coated at 0.5 M NaCl, show the same trend as those coated at 0.05 M NaCl. The Donnan exclusion dominates, which results in the highest retention for CaCl_2 , followed by NaCl and with the lowest retention for Na_2SO_4 . These results are expected due to the positive charge of the PDADMAC terminating layer. However, the membrane from 0.5 M terminated with PSS has a similar trend as its PDADMAC terminated counterpart. This in contrast to the membranes coated at 0.05 M NaCl. It was previously shown that with increasing numbers of layers on a PES support, the $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity was decreased for PDADMAC/PSS layers coated from 1.0 M NaCl.⁴¹ The reason for this is the loss of the negative zeta potential of the PSS terminating layer with increasing amount of bilayers. Also for our PSS terminated membrane with 7 bilayers coated at 0.5 M NaCl, the zeta potential was indeed found to be positive (see the Appendix Chapter 3). This explains that the membrane does not obey a negative Donnan exclusion like behavior, in fact it behaves like an positive membrane. Adusumilli and Bruening showed that after a certain amount of bilayers, a rapid increase in the amount of anion exchange sites within the PEM is formed, for both PSS and PDADMAC terminating layers.⁴¹ This increase in anion exchange sites will facilitate the sulfate transport, thus reducing the retention as observed here. This means that for both the $(\text{PDADMAC}/\text{PSS})_6$ -PDADMAC and $(\text{PDADMAC}/\text{PSS})_7$ membranes coated from 0.5 M NaCl, the diffusion through the multilayer is an important aspect in the rejections of the different ions. These results of both water permeability and ion rejection, show that the properties of PEM modified membranes is not straight forward, but an interplay between the coating conditions, the amount of layers and the terminating layer.

While we have focused so far on explaining the observed salt retentions, it should also be clear that some of the membranes discussed here have good salt retention properties, while retaining a relatively high flux. In one case we obtained a 79% CaCl_2 rejection with a permeability of $10.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-2}\cdot\text{bar}^{-1}$, while another membrane could retain 71% of NaCl and 96% of NaSO_4 with a permeability of $15.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-2}\cdot\text{bar}^{-1}$. This shows again the large potential of polyelectrolyte multilayers to design nanofiltration membranes and control their performance.

3.4 Conclusion

The coating of hollow fiber membranes in a LbL fashion with a polycation and polyanion, can successfully generate nanofiltration membranes with tunable properties. The membrane properties depend very much on the coating conditions, PEM thickness and the terminating layer. Coating at higher salt concentrations yields thicker PEMs per coating step, both on model surfaces as well as on the membranes. Due to the increase in extrinsic charge compensation, PEMs grown at higher salt ionic strength are relatively more open and thus more permeable. We show that on membranes this only becomes apparent when the thickness of these PEMs on the membrane is considered as well.

By systematically changing these parameters, two different regimes of the PEM coated membrane properties have been identified:

- For a thin PEM coated on the hollow fiber, transport of both water and ions is governed by convective flow through the small pores of the membranes. As a result, an increase of PEM swelling leads to lower permeabilities. Additionally, ion rejection is predominantly based on the size of the ion.
- For thicker layers, the solution-diffusion through these layers determines the transport. Layers that are more open, either due to swelling or due to the coating conditions, have higher water permeabilities. The rejection of ions is determined by both the surface and bulk charge of the whole multilayer. This can be controlled by the coating conditions and the amount of monolayers. Counter intuitively, polyanion terminating layers do not always result in negatively charged membranes.

Our results show that for the development of an optimal nanofiltration membrane based on the LbL technique, all of these parameters have to be taken into account. A good understanding of the behavior of these layers, partly obtained from measurements on model surfaces, proofed a powerful tool to control the final membrane properties. This has resulted in membranes with CaCl_2 retentions up to 79%, NaCl retentions up to 71% and Na_2SO_4 retentions up to 96%. Furthermore, simply taking the odd-even effects of the terminating layer on our membrane into account, gives surprisingly much understanding on the transport behavior of the membranes, and on the exact structure of the PEM modified membrane.

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Appendix Chapter 3

A3.1 Coating of Dense HFS Membranes

Fifty dense HFS membrane with a MWCO of 10 kDa, were potted in a module and coated afterwards. Polyelectrolyte solutions (0.1 g·L⁻¹ PE and 0.5 M NaCl) were flown through the inside of the module to ensure coating on the inside of the fibers only. All other coating conditions were kept similar to the coating conditions used to coat the more open fibers. A clear odd-even effect is observed (Figure 7), with higher permeability for PDADMAC terminating layers compared to PSS terminating layers. This indicates that for this dense membrane the layer dominated regime prevails already from the start of the coating experiments.

Figure 7. Permeability after each additional monolayer of a coated dense HFS.

A3.2 Membrane Zeta-potential Measurements

For the determination of the membrane zeta-potential, the coated hollow fiber membranes were potted into a module and the zeta potential was measured with an electrokinetic analyzer SurPASS (Anton Paar, Graz Austria). The zeta potential is calculated by measuring the streaming current versus the pressure in a 5 mM KCl solution at room temperature using the following equation:

$$\zeta = \frac{dI}{dP} \cdot \frac{\eta}{\epsilon \cdot \epsilon_0} \cdot \kappa_B \cdot R \quad (3)$$

where ζ is de zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution (Pa·s), ϵ is the dielectric constant of the electrolyte (-), ϵ_0 is the vacuum permittivity (F·m⁻¹), κ_B bulk electrolyte conductivity (S·m⁻¹), and R is the electrical resistance (Ω) inside the streaming channel. The results of the zeta-potential from different coating conditions are shown in Figure 8.

Figure 8. Membrane zeta-potential after polyelectrolyte addition for 14 layers, coated at different NaCl concentrations.

A3.3 Layer Mass Versus Membrane Permeability

Figure 9. Comparison of PEM mass and membrane permeability for layers coated from different NaCl concentrations: 0.05 M (●) and 0.5 M (■). To exclude any odd-even effects only PDADMAC terminated layers are regarded.

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Swelling Dynamics of Zwitterionic Copolymers: The Effects of Concentration and Type of Anion and Cation
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Swelling Of Zwitterionic Copolymers In Aqueous Solutions

Abstract

The effect of different salts and their concentration on the swelling of zwitterionic copolymers has been investigated for bulk polymer samples as well as for thin films. Relatively low ratios of the zwitterionic monomer already radically change the swelling properties of the copolymer. Increasing the NaCl concentration results in a significant increase of the swelling, which is indicative of the so-called anti-polyelectrolyte effect. The dynamic swelling experiments on the thin film show that only at high NaCl concentrations, the swelling is limited by solute diffusion. These swelling characteristics are distinctly affected by the type of ions present in the aqueous solution. The changes in maximum swelling degree are most sensitive to the type of anion, where the order of the extent of the effect of the anions follows the Hofmeister lyotropic series. For different cations, smaller changes in maximum swelling degree are found that only partially comply with the Hofmeister series. In most cases similar semi-Fickian swelling behavior is found, except in the case of LiCl concentrations above 0.8 M, where anomalous sigmoidal swelling curves are obtained. This behavior in high LiCl concentrations can be explained by the loss of interchain molecular interactions during swelling. This chapter provides meaningful insights on the behavior of zwitterionic copolymer films for applications such as membrane filtration that utilize different ions and ionic strengths.

4.1 Introduction

Zwitterionic polymers are a special class of polymers containing both positive and negative ionic charges. This special characteristic makes this group of polymers an interesting candidate for a variety of applications, ranging from detergents,¹ chromatographic processes and biomedical applications.²⁻³ Thin layers and brushes of such polymers have been shown to reduce cell adhesion and protein adsorption, which is relevant for different biomedical coatings. Furthermore, zwitterionic layers proved to be successful as antifouling layers in different industrial applications.⁴⁻⁷ Especially the latter has resulted in an increased attention for zwitterionic polymers. A particular field where zwitterionic polymers show a large potential is membrane technology, where fouling reduction is critical. In membrane systems, the operating costs and energy consumption are negatively affected by fouling. Membrane fouling results in mandatory downtime of the system and degradation of the membranes due to harsh chemical cleaning steps required. Fouling resistant membranes, based on zwitterionic polymers, may reduce or even prevent the necessity of cleaning, improving the lifetime and operating costs of membrane processes. Furthermore, in dense polymeric membranes (e.g., desalination membranes) the retention of charged low molecular weight solutes (e.g., salts) is determined by the solution-diffusion model.⁸⁻⁹ As a result the retention is, amongst others, a function of the polymer charge.¹⁰ The incorporation of both positive and negative charges via polyzwitterions affects the rejection performance of dense membranes.

4 Another very interesting property that polyzwitterions are known to show is the anti-polyelectrolyte effect: an increase in solubility or swelling of the polymer at increasing salt concentrations.¹¹⁻¹² In addition to zwitterionic polymers, it was recently shown that cross-linked zwitterionic hydrogels also show this antipolyelectrolyte effect.¹³ The reason for this effect is that the addition of ions leads to a screening of the intra- and interchain interactions of the polyzwitterions, resulting in a solubilizing effect. Similar to solubility of proteins and polyelectrolytes, this effect in zwitterionic polymers is dependent on the nature of the specific ions.^{11-12, 14-17} Already in 1888, Hofmeister arranged ions with respect to their ability to precipitate (salt out) egg white from aqueous solutions.¹⁸ Since then, similar trends have been found in numerous reports, including for zwitterionic polymers. Still the mechanism behind this effect is not very well understood.¹⁹ In the case of zwitterionic polymers, the conformation of the polymer chains was shown to be highly sensitive to the asymmetry of the counterion adsorption.²⁰ The anti-polyelectrolyte effect has been linked to anti-fouling behavior,²¹⁻²² and can be explained by an unfavorable entropy of conformation during protein adsorption onto swollen polymer networks.²² Other work has also indicated the importance of electrolyte concentration and the nonspecific adsorption onto zwitterionic films.²³⁻²⁴

Recently a detailed ellipsometric study was performed into the swelling of a thin copolymer film of n-butyl acrylate and SBMA. It was shown that the layer swells significantly in a 1 M NaCl aqueous solution. A key result of this investigation, was that the swelling can cause chain orientation and anisotropy in these thin zwitterionic copolymer films.²⁵ The focus of that work, however, was the development of an optical model to study the swelling. In this work we present the dynamic swelling behavior of zwitterionic copolymers in different aqueous electrolyte solutions. As both the separation performance in membranes and the anti-fouling properties of zwitterionic polymers are dependent on both ion type and concentration,^{10, 26-27} we examined both the static and dynamic swelling behavior of a zwitterionic copolymer for different

electrolytes and concentrations. Since the specific properties of zwitterionic polymers are mainly utilized in thin films or coatings (thickness < 500 nm), we specifically study the effects occurring in thin films using in-situ spectroscopic ellipsometry (SE). SE is a precise and non-destructive measurement technique with a high acquisition rate, which allows the study of the behavior of thin films in the nano- to micrometer range.²⁸⁻³⁰ With the appropriate experimental setup, in-situ swelling experiments can also be performed. The dynamic swelling data are used as input values in the diffusion model developed by Berens and Hopfenberg,³¹ in order to get information on the kinetic sorption behavior of electrolytes in zwitterionic polymer films. The results presented in this study give a better insight in the dynamic interactions of zwitterionic polymers and different aqueous electrolyte solutions, which can be utilized to improve antifouling properties of coatings or enhance the separation properties of dense membranes.

4.2 Theory

Characterization of the Swelling Behavior of Thin Polymer Films

The swelling degree of a polymer film (SD) can be calculated relative to the dry sample thickness as obtained from the in-situ SE experiments. This results in film thickness changes over time that yield information on the kinetics of the swelling behavior of polyzwitterions in the presence of electrolyte solutions. However, the kinetics of polymer swelling are complex. During swelling not only Fickian diffusion behavior takes place, but due to stretching of the polymer, several polymer chain relaxational phenomena will occur as well. Non-Fickian swelling dynamics can be empirically described by a model devised by Berens and Hopfenberg,³¹ which distinguishes between the Fickian and relaxational contributions of swelling and sorption in polymers:

$$SD(t)_{\text{total}} = SD(t)_{\text{Fick}} + SD(t)_{\text{R}} \quad (1)$$

where the ideal Fickian regime is assumed to have a constant diffusion coefficient:

$$SD(t)_{\text{Fick}} = SD_{\text{Fick},\infty} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times e^{\left\{ \frac{D(2n+1)^2 \pi^2 t}{L^2} \right\}} \right] \quad (2)$$

where $SD_{\text{Fick},\infty}$ is the total swelling degree due to Fickian diffusion at infinite time, D is the diffusion coefficient ($\text{cm}^2 \cdot \text{s}^{-1}$), L is the sample thickness (cm) and t is the time (s). The second part of the diffusion relaxation model (equation 1) describes multiple relaxational contributions ($SD(t)_{\text{R}_i}$), and can be quantified according to Equation 3, with the polymer relaxation time constant k_{R_i} (min^{-1}). Often, it is sufficient to limit the number of relaxational contributions to two.

$$SD(t)_{\text{R}} = \sum_{i=1}^{\infty} SD_{\text{R}_i} [1 - e^{\{-k_{\text{R}_i} t\}}] \quad (3)$$

The model is only applicable when the diffusion and relaxational contributions occur at different time scales.³²⁻³³ Since the difference in time scale between Fickian diffusion and

polymer relaxations becomes more prominent for thin films, it is assumed that in our case these processes indeed do not overlap. As already pointed out by other researchers,³⁴ the model lacks a physicochemical explanation of the relaxation phenomena. However, it is useful to compare the swelling and sorption behavior resulting from the diffusion of gasses and liquids into polymer films, in order to get insight in the Fickian diffusion coefficients upon sorption and the relative contributions of Fickian swelling and relaxational phenomena.³⁵⁻⁴⁰

4.3 Experimental

PSBMA-co-nBA Synthesis and Characterization

All chemicals were obtained from Sigma Aldrich (The Netherlands) and used without any further purification steps. For a typical synthesis, 17.4 gram n-butyl acrylate (nBA) (135.7 mmol) and 5 gram N-(3-Sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA) (17.9 mmol) were dissolved in 100 ml DMSO in a 250 ml round bottom flask under a nitrogen atmosphere. For other copolymer ratios, used in the initial swelling experiments, the comonomer ratios were changed accordingly whilst keeping the same total moles of monomer. The solution was heated to 70 °C, subsequently 0.20 gram $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.9 mmol) was added (Figure 1). The mixture was left to react under reflux for at least 12 hours to ensure complete conversion of the monomers. After the reaction, the mixture was poured into demineralized water to form a precipitate. The precipitate was washed three times with 50 ml ultra-pure water for 30 minutes and subsequently dried in a vacuum oven at 30 °C for 24 hours. For further experiments, the polymer was stored under vacuum at 30 °C to prevent water uptake and used without any other purification steps.

Copolymer molecular weight was determined using size exclusion chromatography (SEC) in THF with 0.1 M LiCl against a polystyrene standard. The thermal stability of the copolymer was determined on a PerkinElmer TGA4000 at 20 °C min⁻¹. Differential scanning calorimetry (DSC) was measured on a PerkinElmer DSC8000 at 20 °C min⁻¹. Thin layers were prepared by spin coating the polymer on a piranha (3:1 98% H_2SO_4 : 30% H_2O_2) treated silicon wafer. Spin coating was performed at 2000 rpm for 2 minutes using a solution of 5% of the polymer in 2,2,2-trifluoroethanol (TFE).

Figure 1. PSBMA-co-nBA synthesis via random copolymerisation in DMSO at 70 °C.

The initial swelling experiments were performed by immersing approximately 0.5 grams of dried copolymer in 100 mL of the appropriate solution for at least 24 hours to ensure that the swelling equilibrium has been reached. Before measuring the mass of the swollen polymer, care was taken that any excess solution was removed. The swelling degree was calculated with the swollen weight of the sample as a percentage of the dry polymer mass.

Ellipsometry

Spectroscopic ellipsometry measurements were performed using a Rotating Compensator Ellipsometer (RCE) M-2000X (J. A. Woollam Co., Inc.,) operated in a wavelength range from 370 – 920 nm. The wavelength range used was dictated by significant light absorption by the windows of the test cell below 370 nm, and by water absorption above 920 nm. The time resolution was around 2 seconds per full spectral scan, and the light spot size was about 2 mm. The test cell consisted of glass windows, positioned perpendicularly to the incident light, and the measurements were done at a fixed angle of incidence of 70°. The cell was equipped with a temperature control system, and the temperature was set at 21°C. Before the swelling measurement the film thickness of the dry sample was measured, under nitrogen flow to avoid the influence of moisture. Afterwards the cell was filled with the desired salt solution and the measurement was started within 1 minute after filling the cell. This short period, of approximately 60 seconds, was required for slight corrections of the sample alignment and stabilization of the liquid surface. The ambient refractive index of each salt solution was taken from independent measurements using a standard laboratory refractometer (Carl Zeiss). For a more detailed experimental procedure the reader is referred to our previous work.²⁵ More information about the experimental technique itself can be found in one of the references.²⁸⁻³⁰

The data were fitted dynamically, using an optical model in which uniaxial anisotropy within the thin polymer film was assumed. In the model, a distinction between the in-plane of the sample index (n_{xy}) and the out-of-plane index (n_z) was made and both components were modeled using a simple Cauchy type ($n(\lambda)=A+B/\lambda^2$) optical dispersion, assuming a transparent medium in the range of 370 to 920 nm.

4.4 Results and Discussion

PSBMA-co-nBA Properties and Initial Swelling Experiments

The random copolymerization (Figure 1) results in a slightly tacky, ductile polymer. The overall synthetic procedure gives the PSBMA-co-nBA copolymer at a yield of 89%. The product is still soluble in DMSO due to the relatively low zwitterionic content. Gauthier et al. investigated the reactivity ratios of SBMA and nBA during copolymerization during low and high conversions, and found that although the reactivity ratio of SBMA was higher still random distribution of the copolymers is expected.⁴¹ This means that the composition of the copolymer will be close to the starting monomer ratios. Elemental analysis was used to determine the SBMA content (based on the C-N ratio) in the polymer chain. The SBMA content in copolymer with an initial SBMA monomer concentration of 11.6%, is found to be 11.1 ± 0.07 %, well in line with the starting comonomer composition.

SEC results show that the obtained polymer has a molecular weight average (Mw) of 55,000

Figure 2. Swelling degree of 0.5 gram of PSBMA-co-nBA as a function of SBMA content and for aqueous solutions as indicated. At 18% SBMA, partial dissolution is already occurring in 1 M LiCl, hence the open symbol. Lines are intended as a guide for the eye.

g/mol. No significant weight loss ($< 5\%$) is found until $300\text{ }^{\circ}\text{C}$, while at $450\text{ }^{\circ}\text{C}$ the polymer is found to be completely degraded. DSC measurements indicate the presence of one glass transition temperature (T_g) at $-37\text{ }^{\circ}\text{C}$. The thermal behavior of the copolymer is typical for these kinds of polymers.⁴²

Initial swelling experiments were performed as a function SBMA content (Figure 2). For this, additional polymers with increased SBMA content were synthesized. To obtain the swelling degree (SD), the weight of a small volume of material (0.5 gram) was determined before and directly after immersion in aqueous solution. The copolymer was immersed for at least 24 hours, in solutions containing either pure water, 1 M of NaCl, or 1 M of LiCl. These swelling experiments demonstrate that with a higher content of SBMA a higher degree of swelling is obtained. Moreover, addition of salt leads to a strong increase in the SD, a first indication of the anti-polyelectrolyte effect typical for zwitterionic polymers. Finally, the SD also depends on the type of anion added. The addition of 1 M LiCl leading to a much higher degree of swelling than the addition of an equal quantity of NaCl. For 1 M of LiCl, measurements were only possible up to about 18% SBMA, as above that value the polymer partially or fully dissolved. For 1 M of NaCl, dissolution was observed above 40% of SBMA.

While the above swelling data clearly demonstrate the rich swelling behavior and interesting interactions with salt and the co-polymer under investigation, they were not obtained with the best possible experimental approach and sample geometries representative for possible applications. For the application of zwitterions as anti-fouling layers, but also for the possible use of zwitterions in dense membranes, it is of much greater interest to study the copolymer in the confined geometry of a thin film. Furthermore, the kinetics of swelling are of great interest and could not be measured properly using the weighing technique. For these reasons, swelling of the copolymer was investigated in more detail with spectroscopic ellipsometry. The focus is on a copolymer containing 11.6% of SBMA. For this copolymer, the relative effect of the addition of salt was found to be large (Figure 2), while relative low SD is best suited to the technique of ellipsometry. In addition, the low SBMA content ensures that dissolution of the polymer does not take place, even at high ionic strengths.

Spin coating of the polymer solution in TFE results in uniform films, with thicknesses ranging from 340 to 390 nm. Due to the low T_g , no stress orientations are found in the dry thin films, as measured by ellipsometry. During all swelling experiments, sample integrity is maintained without any dewetting or dissolution of the polymer layers. Spectroscopic ellipsometry reveals that for these polymers, during swelling experiments, relaxation of the polymer can be accompanied by the evolution of significant optical anisotropy of the films. A suitable anisotropic optical model is described and justified elsewhere.²⁵

Swelling Dynamics In Aqueous Solutions Of NaCl

Figure 3 shows the effect of the NaCl concentration on the swelling dynamics of a thin film of the zwitterionic copolymer. A substantially higher swelling degree (SD) is found for increasing electrolyte concentrations, a clear indication of the anti-polyelectrolyte effect. The ions diffusing into the polymer film break up the intra-chain and intra-group ionic interactions. The ion dissociation results in a more hydrophilic nature of the polymer and an increase in swelling of the polymer.¹¹ For our SBMA-nBA copolymer it is especially interesting that, even though the copolymer contains just 11.6% SMBA, we still observe a pronounced and gradual anti-polyelectrolyte effect. The swelling effect is clearly dominated by the SBMA minority, a testament to the high degree of hydrophilicity these groups have at sufficient ionic strength.¹¹

For all concentrations qualitatively similar swelling behavior is observed. In all cases, three distinct contributions can be distinguished: an initial fast Fickian region, a positive relaxational contribution, and a subsequent slight decrease in SD due to secondary relaxations and orientation of the polymer chains.²⁵ The decrease of the SD typically manifests after prolonged swelling, as shown in Figure 3b. The magnitude and rate of the different contributions are dependent on the actual NaCl concentration. Table 1 shows the Fickian diffusion coefficients and the relaxational contributions, extracted from the kinetic swelling data of Figure 3 using the Berens-Hopfenberg relation.³¹

In these measurements, data acquisition was always started 60 seconds after exposure to the aqueous solution. This to allow for slight corrections of the sample alignment and stabilization of the liquid surface. Although we realize we exclude the initial measurement data from our

Figure 3. Effect of NaCl concentration on the swelling of thin PSBMA-co-nBA films; A) 0-0.8 M; B) 0.8-3.0 M NaCl.

Table 1: Film thicknesses, Fickian diffusion coefficients and relaxational contributions as obtained from the Berens-Hopfenberg model for different [NaCl].

[NaCl] (M)	d_0 (nm)	D (cm ² /s)	SD_{Fick}	SD_{R1}	SD_{R2}	k_{R1} (min ⁻¹)	k_{R2} (min ⁻¹)
0	369	$> 1 \cdot 10^{-8}$	x	x	X	x	x
0.2	343	$3 \cdot 10^{-10}$	44.7	9.2	-6.4	1.54	$6 \cdot 10^{-2}$
0.4	371	$6 \cdot 10^{-12}$	62.7	14.7	-17.0	0.32	$2 \cdot 10^{-2}$
0.6	382	$5 \cdot 10^{-12}$	66.9	16.9	-27.0	0.19	$5 \cdot 10^{-3}$
0.8	340	$5 \cdot 10^{-12}$	76.2	15.7	-39.2	0.17	$2 \cdot 10^{-3}$
1.0	330.	$4 \cdot 10^{-12}$	83.5	23.3	-12.8	0.08	$8 \cdot 10^{-2}$

d_0 = dry film thickness; D = diffusion coefficient; SD_{Fick} = Fickian swelling contribution; SD_{Ri} = polymer relaxational contribution; k_{Ri} = polymer relaxational time constant

analysis, the data still include the most relevant time span as it includes the curvature of the Fickian diffusional component needed to accurately and reliably calculate the Fickian diffusion. In the situations where this was not the case, for example for pure water, the reported values provide a minimum value for the Fickian diffusion coefficient. For concentrations up to 1.0 M NaCl, the experimental results can be very well described with the empirical correlation of Berens and Hopfenberg, indicating that the Fickian contribution and the two relaxational terms (a positive one and a negative one) are sufficient to describe the experimental observations. A representative example of a fit is given in Figure 4. The results show apparent differences between the time scales of the different processes. The Fickian contribution manifests itself in the first minutes, while both the positive and negative relaxations are significantly slower and become more pronounced at longer time scales. The contribution of the Fickian swelling goes up with increasing concentration, due to a more pronounced anti-polyelectrolyte effect. Although the swelling at the start of data acquisition ($t = 60$ s) increases with increasing NaCl concentration, the diffusion coefficients are relatively stable in this range of concentrations, indicating no concentration dependence on the diffusion coefficient through the polymer films. At concentrations above 1 M NaCl the results suggest a change in the characteristics of the swelling dynamics (Figure 3b). First of all, at concentrations above 1M NaCl, the initial swelling rate (after 60 s) is reduced, even though the maximum swelling degree continues to increase up to 3 M. This effect can be attributed to concentration dependence of the diffusion coefficient. It is known that both water and ion diffusivity significantly decrease at higher salt concentrations in water and matrices.⁴³⁻⁴⁵ We therefore suggest that at the higher concentrations, the pronounced diffusion limitations prolong the timescale of initial swelling, causing it to overlap more with the timescale of (in particular the positive) relaxation. The diffusion limitations are associated with the development of non-linear concentration profiles inside the film.⁴⁶ Modeling results of the raw optical data from spectroscopic ellipsometry indeed suggest the existence of a salinity gradient through the thickness of the film at the initial stages.²⁵ The existence of a salinity gradient

Figure 4. Fickian and relaxational contributions of the total swelling of the film. Experimental results are also shown (O); $[\text{NaCl}] = 0.6 \text{ M}$.

also implies a variation of the diffusion coefficient over the film, consequently the Berens-Hopfenberg diffusion-relaxation model is no longer valid at higher concentrations ($>1.0 \text{ M}$). In agreement with this, at concentrations above 1 M , the initial swelling dynamics are not described well by a Fickian diffusion, a single positive relaxation, and a negative relaxation (fitting results are not shown). These effects are more pronounced at higher NaCl concentrations. A second positive relaxation has to be added to obtain an adequate fit, limiting the physical significance of the fitting parameters.

The observed anti-polyelectrolyte effect, and the connected strong dependence of the swelling on the ionic strength, make this copolymer very interesting for certain dense membrane applications. The hydration of such a dense layer membrane is a key parameter in its retention behavior, with more swollen layers allowing larger molecules to pass through the membrane.⁴⁷ With this polymer it thus becomes possible to build a responsive membrane, where the ionic strength can be a control parameter for its swelling and retention behavior. While such responsive membranes exist, they are usually based on polyelectrolyte behavior, with a higher ionic strength leading to a collapse of the layer.⁴⁸⁻⁴⁹ Zwitterion based membranes would have a unique inverse dependence on the ionic strength.

Several researchers have pointed out the correlation between the ionic strength and the anti-fouling behavior of zwitterionic polymers.²²⁻²⁴ The observed increase in swelling with NaCl concentration in our system is in all cases accompanied by polymer chain orientations,²⁵ and this may subsequently result in increased antifouling effects at higher ionic strengths according to the theory of Ruhe and co-workers.²² This is supported by the increased nonspecific adsorption at higher ionic strengths as observed by Zhang et al.²⁶ If the interactions between foulants, e.g., proteins, and the zwitterionic polymer are weak, the contribution of enthalpy to the change in free energy upon adsorption is small. Variations in the free energy of the adsorption process are in this case mainly entropy driven. This is also the case for swollen neutral networks or swollen charged networks from strong polyelectrolytes.²² During adsorption, the entropy of mixing is opposed by loss of conformational entropy of the polymer chains. The loss of conformational entropy is referred to as 'entropic shielding'. With sufficient entropic shielding, adsorption or fouling, becomes unfavorable. Here we show that the relative change in swelling degree is the highest at lower NaCl concentrations, and subsequently the change in entropic shielding will thus most sensitive at the lower NaCl concentrations. This is in accordance with results which

show that, although an increase in ionic strength will result in reduced adsorption over a wide ionic strength range, this reduction in adsorption is most sensitive at low ionic strengths.^{22, 26}

Effect of Type of Ion on the Swelling Degree

Zwitterionic polymers are known to behave differently in electrolyte solutions containing different ionic species.^{11, 14-17} For the zwitterionic PSBMA-co-nBA thin films, this is apparent from the differences in dynamic swelling in electrolyte solutions with different anions (Figure 5) (cation Na^+) and different cations (Figure 6) (anion Cl^-). Figure 5 shows that the response of the zwitterionic polymer is very sensitive to the type of anion for sodium salts at 1 M. In additional experiments at different concentrations, an identical order in the sensitivity was observed. The observed order of the magnitude of swelling, for the anions, is:

$$\text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{I}^-$$

This order is similar to trends found by other researchers, although sulfate was not regarded in any of those cases.^{11, 14-17} There is no consensus on the rationalization of this order, which must be linked to the complex electrostatic interactions of the electrolytes, water and the zwitterionic groups on the polymer chain. It cannot be readily explained based on the size, either by the crystalline radii or the hydrated radii of the different ions (Table 2). A slight correlation can be seen with the Stokes radii, especially for the considerable differences between the halogens and the sulfate ion. However, the differences in Stokes radii for the halogens are relatively small compared to the differences in swelling degree. Lee et al. attributed the solubility power of anions to the ratio of charge to radius,¹⁶ and although this theory holds for the monovalent anions, it fails for the divalent sulfate.

The magnitude of swelling does follows the well-known empirical Hofmeister lyotropic series: the ability of a salt to precipitate a protein or polyelectrolyte from water.^{18, 52} For a certain concentration of anion, the lyotropic series (in their ability to salt out a polyelectrolyte) is as follows:

Figure 5. Effect of type of anion on the swelling dynamics of thin PSBMA-co-nBA films at 1M Na^+ .

Figure 6. Effect of type of cation on the swelling of thin PSBMA-co-nBA films. All concentrations are 0.4 M.

Table 2: Comparison of the maximum SD of thin PSBMA-co-nBA films for different anions and cations and their corresponding radii. ^a $I = 1.5$ M, ^b $I = 1$ M, ^c 0.4 M (I = ionic strength).

	Ion	$SD_{\max}$ (%)	Crystal ionic radii (nm) ⁵⁰	Stokes radii (nm) ⁵¹	Hydrated Radii (nm) ⁵¹
Anions	SO_4^{2-}	35.5 ^a	0.290	0.230	0.379
	Cl^-	96.2 ^b	0.181	0.121	0.332
	Br^-	118.5 ^b	0.196	0.118	0.330
	I^-	133.2 ^b	0.220	0.119	0.331
Cations	Li^+	64.4 ^c	0.060	0.238	0.382
	Na^+	74.3 ^c	0.095	0.184	0.358
	K^+	77.5 ^c	0.133	0.125	0.331
	Ca^{2+}	80.9 ^c	0.099	0.310	0.329

Although a complete understanding of the mechanism behind the effect of different ions from the series is not yet obtained,¹⁹ it is thought to be due to changes in the water structure at the interface of the polymer or protein in the presence of different ions, leading to changes in chain conformations and subsequently to precipitation.^{19, 52} We assume that similar interfacial mechanisms between water, ions and the zwitterionic polymer are responsible for the changes in SD that we observed for different aqueous electrolyte systems.

In addition to the type of anion, also the effects of the type of cation (with a similar anion (Cl^-)) on the swelling dynamics has been investigated (Figure 6). The swelling dynamics also depend on the type of cation, although the observed differences are less pronounced as compared to the anions. Such relatively less pronounced effects induced by cations, as compared to anions, have been observed before for polyelectrolytes,⁵² and polyzwitterions.^{14, 17}

Unlike for the different anions, the order of the swelling per cation depends on the ion concentration. At concentrations below 0.8 M, the order of the swelling per cation is:

$$Li^+ < Na^+ < K^+ < Ca^{2+}$$

The order of the swelling of cations does follow the Hofmeister series for the monovalent ions, but Ca^{2+} is a clear trend breaker. For cations the, less well defined, Hofmeister series is:⁵²

The results obtained in our dynamic swelling experiments on copolymers, can be compared to the results for the solubility of homopolymers of sulfobetaines in different electrolyte systems. In the case of homopolymers there exists a critical (θ) salt concentration above which the polymers

become soluble in water. Comparable trends as presented here were found by Lee et al. for all the cations measured,¹⁶ by Salamone et al.¹⁵ for just the monovalent ions, and by Wielema et al.¹⁴ for the alkaline metal chlorides. Nevertheless, other orders for the cations have also been found,¹⁵ with the order being sensitive to differences in concentrations of both homopolymer and ions.¹¹

The reason that Ca^{2+} is found to be a trend breaker is likely due to its valence. Bivalent cations, and especially Ca^{2+} , are known to have increased interactions with organic ions.⁵³ However, it was also shown that in the case of organic sulfonates, the interaction with calcium is slightly less compared to sodium.⁵⁴ Typically, the same molar concentrations of the salt (and thus cations) are used. For divalent cations this means that at a certain concentration of cation, double the amount of the anion Cl^- is present. Since the influence of anion is usually more significant as compared to that of cations (see also Figure 5), this complicates comparison between cations with different valences. The extra Cl^- can easily explain the relatively high level of swelling observed for Ca^{2+} , and thus why Ca^{2+} does not follow the Hofmeister series.

At higher concentrations, the cation order with respect to swelling degree changes (Figure 7). This change is mainly due to a change in the behavior of LiCl and manifests at concentration above 0.8 M LiCl . Such a change is in accordance with the findings of Schultz et al, who concluded that the cation order for solubility is a function of the concentration ratio between the polymer and electrolyte and showed a significant concentration dependence for lithium salts.¹¹ The change in degree of swelling of LiCl above 0.8 M is accompanied by a striking change in swelling dynamics from a semi-Fickian-like to a sigmoidal swelling behavior (see Figure 7b). Sigmoidal swelling in polymers is often attributed to the superposition of simultaneous processes.^{46,55} One of these processes may be a loss in strength of the interactions between the polymer chains. The anomalous swelling observed for lithium is not found for the other electrolyte systems. Even at significantly higher concentrations and consequently higher swelling degrees, Fickian-like curves are observed for the other electrolytes (up to 3 M NaCl). This means that the sigmoidal swelling cannot be attributed solely to ductile failure of the material, as has been suggested for other polymer systems.⁵⁵ According to Diez-Pena et al., the sigmoidal behavior could be caused by an autocatalytic water up-take mechanism, where the uptake of the first water molecules aids in the uptake of the next ones.⁵⁶ A comparable behavior has been found for a copolymer of methacrylic

Figure 7. The effect of electrolyte concentration on the swelling of thin PSBMA-co-nBA films. A) Maximum swelling degree for a range of concentrations for different chloride salts (LiCl = ●, NaCl = □, KCl = ○, CaCl_2 = ▲); B) Change of swelling dynamics in LiCl solutions from 0.8 to 1.2 M.

acid with an poly(ethylene glycol) side chain, where an increase in pH and the subsequent ionization of the carboxylic groups leads to the loss of hydrogen bonds between the polymer chains.⁵⁷ Similar to this, a high lithium concentration may result in a complete deionization of the SO_3^- group in the polymer chain, significantly reducing the interchain interactions. To confirm this, swelling experiments were also done at different HCl concentrations, both above and below the pK_a of the SO_3^- group. However, even at a pH as low as 0.1 no sigmoidal behavior was observed and the swelling dynamics were comparable to all other experiments. Most probably, the solvation shell around the lithium, and consequently the water structure at the surface of the polymer, changes at high lithium concentration.⁵⁸ This may result in a complete loss of intermolecular polymer chain interactions, and thus extended swelling degrees. Much work has already been done to comprehend the solvation of lithium in water.^{44, 59-60} Egorov et al. used molecular dynamic simulations to show that lithium fits well in the hydrogen bonded water network.⁴⁴ However, at higher concentrations of LiCl, the tetrahedral network can deteriorate.⁶⁰ These results indicate that indeed the solvation of lithium may change at higher concentrations. Still, a full explanation of this in the complex matrix of water, zwitterionic polymer and LiCl is lacking. Our results do suggest a change in electrostatic interactions between the polymer chain upon the onset of the sigmoidal swelling, as the anisotropy observed for all experiments²⁵ is lost during the sigmoidal expansion and a fully isotropic swollen layer is obtained.

The significant differences in swelling of the PSBMA-*co*-nBA copolymer film indicate a potential use as an ion-selective membrane. Ions that have a high affinity for a membrane might selectively pass through that membrane. For our copolymer layer, there is a very unfavorable component to swelling of the copolymer layer, as increased swelling brings more of the hydrophobic nBA groups in direct contact with water. A higher degree of swelling must thus be compensated by a higher affinity of the ions for the SBMA groups to overcome these unfavorable solvent interactions. Our data thus indicates that the zwitterion copolymer has a different affinity for several ions, which could be an excellent basis for a membrane separation process.

The significant differences in the effect of the concentration and the type of anion and cation can be used in antifouling studies, as interactions between the electrolytes in solution and zwitterionic polymers determine the antifouling behavior of zwitterionic layers.²²⁻²⁴ We therefore reason that fouling will be dependent on the type of electrolyte in the environment, similar to the ionic strength being coupled to the anti-polyelectrolyte effect and the anti-fouling behavior. However, to the best of our knowledge no extensive data exist on the fouling rate of zwitterionic films in different electrolyte solutions.

4.5 Conclusion

In this chapter we evaluated the kinetic swelling behavior of zwitterionic thin films from PSBMA-*co*-nBA. The diffusion/relaxation model has been used to quantify the semi-Fickian swelling dynamics, distinguishing between solute diffusion and polymer chain relaxations. A significant dependence of the swelling degree and dynamics on the NaCl concentration is found. At higher NaCl concentrations the swelling degree and rate both increase, corresponding to a more pronounced anti-polyelectrolyte effect. The value of the diffusion coefficient, obtained from the Berens-Hopfenberg model remains constant. At NaCl concentrations above 1 M, the diffusion coefficient decreases, causing diffusion and relaxation of the polymer processes to overlap.

Furthermore, the results clearly show a dependence on the type of ion on the swelling dynamics. The effects are most pronounced for anions, and are in accordance with the well-known Hofmeister series. For varying types of cations, less significant effects are found and these do not comply with the Hofmeister series. LiCl shows an anomalous behavior at concentrations above 0.8M. Sigmoidal swelling curves indicate additional loss of intermolecular polymer chain interactions during swelling. This is supported by the distinct evolution of the materials anisotropy at the higher LiCl concentrations, as derived from spectroscopic ellipsometry.

The above results indicate that the PSBMA-*co*-nBA copolymer under investigation has a real potential as a material for dense membranes. The observed anti-polyelectrolyte effect could be the basis for a responsive membrane, for which hydration and thus the retention behavior are controlled by the ion type and concentration. Furthermore, the significant differences in swelling for different ion-types indicate a potential use of this copolymer as an ion selective membrane. Finally, copolymers containing zwitterion groups are known to exhibit excellent anti-fouling properties, an added benefit to using the copolymer for membrane applications.

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Zwitterionic Polyelectrolyte Multilayers For Responsive Membranes

Abstract

In this chapter, we systematically investigate the assembly of multilayers based on a polyzwitterion (PSBMA) and a polycation (PDADMAC) for the development of ionic strength responsive membranes. Although the polyzwitterion is essentially charge neutral, we show that specific electrostatic interactions with the PDADMAC allow for the formation of stable multilayers. The growth of this LbL system is monitored on model surfaces (silica) via optical reflectometry for different pH values and ionic strengths. While no effect of pH on the layer growth is observed, we did observe a strong dependence on the ionic strength. Upon increasing the ionic strength during deposition from 0.005 to 0.5 M NaCl, the adsorbed amount is significantly decreased, a behavior that is opposite to classical LbL systems. Similar results to those obtained on silica, are also observed on top of classical LbL systems and on polymeric membranes. This demonstrates that the growth of the polyzwitterion multilayers is independent of the substrate. Coating these polyzwitterion multilayers on hollow fiber membranes via dip-coating, yields membranes that are stimuli responsive toward the ionic strength of the filtration solution, with an increase in permeability of up to 108% from 0 to 1.5 M NaCl. We show that the fabrication of the polyzwitterion multilayers is an easy and controlled way to provide surfaces, such as membranes, with the specific functionalities of polyzwitterions.

5.1 Introduction

Responsive polymeric systems have received wide attention over the years with a multitude of applications including controlled molecular transport,¹ fouling control,²⁻³ (nano)sensors, and drug delivery.⁴⁻⁶ Out of the possible applications, membrane based separation processes, with separation at a molecular scale, are very promising areas for these polymeric systems.⁷ A reversible increase in the membrane permeability can for instance be used to increase the convective flow during a backwash of the membrane in order to enhance the effectiveness of the backwash. Several approaches have been taken to render membranes or membrane materials stimuli-responsive. Unfortunately, these methods typically require organic solvents and chemical reactions to graft the responsive polymer to the substrate in a stable manner.⁶ A more mild approach is photoinitiation or plasmainitiation, usually operated in aqueous environments. However, this can be accompanied by substantial substrate degradation,⁸ which is inherent to the grafting process. Furthermore, this approach is limited to the modification of the outside of the membrane surface and as such necessitates the use of flat sheet membranes or the outside-to-in filtration of hollow fiber membranes. An ideal membrane modification method to make membranes stimuli-responsive should allow for modification of all membrane geometries without the use of any harsh chemicals, organic solvents, or invasive treatments.

5 A more facile membrane modification method that does not require a harsh chemical reaction is the deposition of polyelectrolyte multilayers (PEMs) via the layer-by-layer (LbL) approach.⁹⁻¹⁰ In this approach, alternating between the deposition of polyanions and polycations leads to a very well-defined multilayer system. While most of the research on the layer-by-layer buildup has been performed on model surfaces, it has already been proven that these layers can be transformed to functional membranes.¹⁰⁻¹⁴ By carefully choosing the number of layers and by changing the coating conditions, the properties of the PEMs can be precisely controlled.¹⁵⁻¹⁷ In addition, by choosing the appropriate polyelectrolytes, the PEMs can be made stimuli-responsive.¹⁸⁻¹⁹ PEMs from weak polyelectrolytes, such as poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH), change their thickness upon changes in pH by protonation and deprotonation.²⁰ By incorporation of the well-known temperature responsive poly(N-isopropylacrylamide) (PNIPAM),^{1, 21-22} the PEMs become responsive to the temperature as well.²³ A stimuli that has received far less attention in the case of PEMs, is the ionic strength. While the ionic strength is often employed to control the PEM structure and thickness during the multilayer buildup, once PEMs have been prepared, they generally do not show significant changes in thickness as function of the ionic strengths over a wide concentration range after formation.²⁴ It is however known that the properties of the multilayers can alter after preparation when exposed to very high ionic strengths. Dubas et al. showed that the surface roughness of a PEM can be reduced by exposing the layer to 0.5 M NaCl.²⁵ It was also shown by Han et al. that at even higher salt concentrations (>3 M NaCl), the layers started to decompose.²⁶ Although the loss of (part of the) layer can be used in for instance cleaning procedures for surfaces,²⁷ it is not reversible and can thus not be utilized for stimuli-responsive layers. The building of PEMs at high ionic strengths (3 M) can lead to reversible thickness changes upon switching between low and high salinities.²⁴

Polyzwitterions, charged polymers with both a positive and negative moiety on the same repeating unit, are polymers that are known to have a strong response to changes in ionic strength and are thus expected to be suitable to make ionic strength responsive membranes. Polyzwitterions show an anti-polyelectrolyte effect: an increase in solubility and/or swelling with increasing

ionic strengths.²⁸ Although they are commonly used in antifouling applications, their anti-polyelectrolyte effect also gives potential for ionic strength based responsive behavior. This can for instance be used in chromatography for the separation and isolation of proteins.²⁹ Zhai et al. grafted the zwitterion N,N'-dimethyl-(methacryloyl ethyl) ammonium propanesulfonate (DMAPS) to poly(vinylene fluoride) for electrolyte-responsive microfiltration membranes.³⁰ Because of the anti-polyelectrolyte effect, the polyzwitterions swell and block the pores at high NaCl concentrations, leading to a reduced permeability.

In this chapter, we will incorporate a zwitterionic polymer in the layer-by-layer technique to make electrolyte-responsive membranes. Although a polyzwitterion contains ionic charges, its net charge is neutral. This means that the growth of PEMs with polyzwitterions follows a complex mechanism, which may not solely rely on charge-charge interactions. Kharlampieva et al. investigated the assembly of the weak polyzwitterion polycarboxybetaine with polyanions.³¹ Only below certain critical pH levels -due to the protonation of the carboxylic acid- the multilayers were formed and found to be stable. Later, Kharlampieva et al. also investigated the layer assembly of the polycarboxybetaine with the neutral poly(N-vinylcaprolactam).³² The nature of the interactions of the subsequent layers is not classical ion-ion based, but based on hydrogen bond acceptors and donors. Again, the layers were only self-assembled and stable at low pH values, where the protonated carboxylic groups of the zwitterionic polymer can act as a hydrogen bond donor. Comparable results were obtained by Gui et al.³³⁻³⁴ Strong zwitterionic polymers, on the other hand, like polysulfobetaine, got less attention. Nevertheless, the growth of multilayers with polysulfobetaine at very low pH values has been investigated.³⁵⁻³⁶ At extreme pH values (pH < 1), the sulfonate group becomes protonated, effectively rendering the sulfobetaine a polycation. The temperature stability of similar systems was also investigated, showing a critical disintegration temperature which is dependent on pH.³⁷ For both these systems, the deprotonation of the anionic moieties will contribute to the layer loss at higher pHs, thus limiting the application of such systems. Moreover, as the above layers were only stable after protonation of the carboxylic acid or the sulfonate group, the layers did not contain a true zwitterion. This can be overcome by making a layer based on a strong zwitterionic polymer at a less extreme pH, where the polyzwitterion has both positive and negative charges.

In this chapter we present the building of multilayers on silicon surfaces of the polysulfobetaine poly(N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine) (PSBMA) and poly(diallyldimethylammonium chloride) (PDADMAC), see Figure 1, under various coating conditions. It was shown by Mary et al. that these polymers show specific interactions, but no excessive study on the multilayer growth has been performed.³⁸⁻³⁹ We monitor the multilayer growth of the PDADMAC and PSBMA in-situ by means of reflectometry. We systematically change the ionic strength and pH of the coating solutions to investigate their effects on the adsorbed amount of polymer and on the stability of the multilayer system. At all the conditions used in this work, the polyzwitterion keeps its true zwitterionic nature, in contrast to the research mentioned earlier. In order to demonstrate the versatility of the system, the sulfobetaines-based multilayer is also grown on a traditional multilayer system (PDADMAC and poly(styrene sulfonate) (PSS)). We then apply these multilayer systems on to functional hollow fiber membranes as well. The permeability of the membranes is subsequently tested at various ionic strengths in order to assess the layer stability and the stimuli-responsive behavior of the system.

Figure 1. Chemical structures of the different polymers.

5.2 Experimental

Chemicals

N-(3-Sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA) was obtained from Sigma Aldrich (The Netherlands). Poly(diallyldimethylammonium chloride) (PDADMAC, Mw = 150 kDa, 20 wt% in water) was obtained from Kemira (Finland). Polystyrene sulfonic acid (PSS, Mw = 100 kDa, 20 wt% in water) was obtained from Tosoh Organic Chemical Co., LTD (Japan). All other chemicals were purchased from Sigma Aldrich (The Netherlands). All chemicals were used without any further purification steps.

Polymer Synthesis and Characterization

For a typical homopolymer PSBMA synthesis, 500 mL demineralized H₂O was flushed with nitrogen for 1 h in a 1000 mL round bottom flask. In this, 54.6 gram (195 mmol) SBMA was dissolved under a nitrogen atmosphere. The solution was heated to 50 °C, subsequently 0.92 gram (4.0 mmol) (NH₄)₂S₂O₈ was added. The mixture was left to react under a nitrogen atmosphere for 15 hours. After the reaction, the mixture was cooled and poured into MeOH to form a precipitate. The precipitate was washed three times with 100 mL acetone and subsequently dried in a vacuum oven at 30 °C for 24 h. For further experiments, the polymer was stored under vacuum at 30 °C to prevent water uptake and was used without any other purification steps. The PSBMA structure was verified with ¹H-NMR (see Appendix Chapter 5). The molecular weight was determined via MALLS with a 1.0 g·L⁻¹ PSBMA solution in 0.2 M NaCl. The density of the PSBMA was measured on a Micromeritics AccuPycII 1340 helium pycnometer.

Multilayer Growth

The multilayer growth on plasma treated silicon wafers was monitored by means of reflectometry.⁴⁰ For this, 0.1 g·L⁻¹ polymer solutions with ionic strengths varying between 0.005 and 0.5 M NaCl were prepared and alternatively adsorbed at room temperature on a silicon wafer with a 75 nm SiO₂ top layer. The different solutions were applied to the silicon wafer until a stable adsorption plateau was formed. The use of a stagnation point flow cell allows for very well controlled hydrodynamics during the multilayer growth.⁴¹ In reflectometry, polarized monochromatic light (He-Ne laser, 632.8 nm) hits the wafer around the Brewster angle (71°) and is reflected towards

the detector. The reflected light is split into its p- and s- polarized components. The ratio between the change in these components (ΔS) is directly proportional to the amount of mass adsorbed to the wafer, according to equation 1:

$$\Gamma = \frac{\Delta S}{S_0} Q \quad (1)$$

where Γ is the amount of mass adsorbed on the wafer ($\text{mg}\cdot\text{m}^{-2}$) and S_0 is the starting output signal of the bare silicon wafer (-). Q is a sensitivity factor, which depends on the angle of incidence of the laser (θ), the refractive indices (n), the thicknesses (d) of the layers on the silicon wafer, and the refractive index increment (dn/dc) of the adsorbate. To calculate the Q -factor an optical model was used, based on the following values: $\theta = 71^\circ$, $n_{\text{silica}} = 1.46$, $\bar{n}_{\text{silicon}} = (3.85, 0.02)$, $n_{\text{H}_2\text{O}} = 1.33$, $\text{dn}/\text{dc}_{\text{PDADMAC}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, $\text{dn}/\text{dc}_{\text{PSS}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, and $d_{\text{silica}} = 75 \text{ nm}$.²⁷ For the PSBMA the $\text{dn}/\text{dc}_{\text{PSBMA}}$ was found to be $0.14 \text{ mL}\cdot\text{g}^{-1}$. This leads to slightly different Q -factors for the different polymers. For the sake of simplicity we used the average of these Q -factors ($30 \text{ mg}\cdot\text{m}^{-2}$) for all our experiments, weighted for the observed higher adsorption of PSBMA (see results section). There are some limitations to the validity of the Q -factor in case of multilayer systems,⁴² as counterion release upon complexation makes it difficult to know the exact refractive index increment of the polymers. We therefore emphasize that the absolute numbers might be off by a margin of 15% (high estimate), but that the relative numbers can be compared in a very good way. To support our theoretical Q factor, we also measured the thickness of some dry layers by AFM (scratch technique). The thicknesses of PDADMAC/PSBMA bilayers grown on a silicon wafer were 5.5, 3.5, and 1.6 nm for 0.05, 0.2 and 0.5 M NaCl. These thicknesses, assuming an average layer density of $1.3 \text{ g}\cdot\text{cm}^{-3}$, translate to 7.2, 4.6, and $2.08 \text{ mg}\cdot\text{m}^{-2}$ respectively, which is in good agreement with the reflectometry results of 6.8, 2.7, and $1.5 \text{ mg}\cdot\text{m}^{-2}$. In addition AFM was also used to measure the roughness of the layers.

Polymeric Hollow Fiber Membrane Modification and Performance

For the multilayer membrane design, polymeric hollow fiber membranes (Hollow Fiber Silica (HFS) membranes) were kindly provided by Pentair X-Flow in Enschede, The Netherlands. These membranes are tight ultrafiltration membranes designed for the removal of silica from water, are based on sulfonated polyethersulfone (SPES) and have a molecular weight cut-off of 10kDa. The membranes are asymmetric and are designed for inside-out filtration (scanning electron microscope images are available in the Supporting Information). Prior to the layer-by-layer modification, the fibers were immersed in water for at least 16 h to completely wet the fibers. The fibers were then immersed in a $0.1 \text{ g}\cdot\text{L}^{-1}$ polycation solution with the appropriate NaCl concentration. After 1 h, the fibers were subsequently rinsed in 3 different NaCl solutions with identical ionic strength, and a membrane sample was taken. The remaining samples were, in an alternating fashion, dipped in PSBMA (or PSS) and PDADMAC solutions, taking a sample after each coating step. After rinsing, all membrane samples were put in a glycerol/water mixture for 4 h and dried overnight. Single PEM coated membrane fibers were potted in a module with a fiber length of approximately 200 mm for the filtration experiments. The permeability ($\text{in L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) was calculated by normalizing the measured membrane flux with the trans membrane pressure. The membrane resistance was calculated with equation 2:

$$R = \frac{\Delta P}{\mu \times J} \quad (2)$$

with the membrane resistance R in m^{-1} , J the membrane flux in $\text{m}\cdot\text{s}^{-1}$, μ the dynamic viscosity in $\text{Pa}\cdot\text{s}$ and ΔP the trans membrane pressure in Pa . During the filtration experiments, the temperature of the liquids was measured and kept constant at room temperature in order to avoid viscosity changes of the water.

Membrane Zeta-potential Measurements

The membrane zeta potential measurements were performed with an electrokinetic analyzer SurPASS (Anton Paar, Graz Austria). The zeta potential was calculated by measuring the streaming current versus the pressure in a 5 mM KCl solution at room temperature and the following equation:

$$\zeta = \frac{dI}{dP} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \kappa_B \cdot R \quad (3)$$

where ζ is the zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution ($\text{Pa}\cdot\text{s}$), ε is the dielectric constant of the electrolyte (-), ε_0 is the vacuum permittivity (F m^{-1}), κ_B is the bulk electrolyte conductivity ($\text{S}\cdot\text{m}^{-1}$), and R is the electrical resistance (Ω) inside the streaming channel. For each point, the zeta-potential is measured four times for two different membranes and the average and standard deviation is reported.

5.3 Results and Discussion

PSBMA Properties

The overall yield of the polymer synthesis was around 77% and yields a hygroscopic material which is brittle when dry. To prevent any water uptake during storage, the polymer is stored in a vacuum oven at 30 °C. The density of the dried PSBMA, as measured via pycnometry, is $1.3938 \pm 0.0016 \text{ g/cm}^3$. The solubility of the PSBMA is characteristic for polyzwitterions,²⁸ 0.1 $\text{g}\cdot\text{L}^{-1}$ PSBMA is not soluble below 5 mM NaCl aqueous solutions. At higher salt concentrations (up to 1 M NaCl), clear solutions are obtained. The dn/dC of the PSBMA was found to be 0.14 mL/g at 0.2 M NaCl, comparable with previous results.⁴³ This factor was used to quantify both the MALLS and reflectometry experiments. The PSBMA has a molecular weight of 500 kDa and a radius of gyration of 34 nm, as determined by MALLS in 0.2 M NaCl.

A simple interaction experiment between the PSBMA and polyelectrolytes, by mixing 1.0 $\text{g}\cdot\text{L}^{-1}$ aqueous polymer solutions, visually shows the presence of PDADMAC/PSBMA complexes by a significant increase in the turbidity of the mixture. However, no such evidence was found for interactions between PSS and PSBMA. We confirm this selective interaction behavior of SBMA by adsorption experiments with reflectometry: PSBMA was found to adsorb onto PDADMAC layers but not onto PSS layers. A possible explanation for these selective interactions was pointed out by Mary et al.³⁹ The PSBMA can undergo partial hydrolysis (between 11 and 15%) at the ester bond during synthesis to yield acrylic acid (AA). These amounts of hydrolysis are expected to have a considerable effect on the building and properties of the formed multilayers, as the additional negative AA moiety will change the interactions with our polycation. In our case, however, ^1H -NMR analysis of the polymer (in 1 M NaCl/ D_2O) did not provide any evidence for the occurrence of a significant hydrolysis of the SBMA during synthesis.

Figure 2. A typical reflectometry graph showing the subsequent adsorption of PDADMAC (+) ($0.1 \text{ g}\cdot\text{L}^{-1}$) and PSBMA (z) ($0.1 \text{ g}\cdot\text{L}^{-1}$) in 0.5 M NaCl at pH 3.4. Flushing with a background electrolyte solution (0.5 M NaCl) is indicated with “s”.

Multilayer Growth

A typical result from the reflectometry experiments is shown in Figure 2. In these experiments we measure the adsorbed amount of polymer as a function of time, while we alternate between the adsorption of PDADMAC (+) and PSBMA (z). Before switching between the polymer solutions, a switch was always made to a background electrolyte solution (s) to exclude the possibility of bulk mixing of PSBMA and PDADMAC. Our experiment clearly shows that PDADMAC/PSBMA multilayers can be assembled in a LbL fashion. Initially, the assembly is characterized by a strong increase in layer mass per adsorption step, but after 8-10 adsorption steps we seem to reach a plateau in adsorbed amount. Furthermore, the multilayer growth presented here shows a strong odd-even effect with respect to the adsorption behavior of the two different polymers. Although the layer thickness increases with each PSBMA step, during the PDADMAC step part of the multilayer is lost, a behavior that is different than that of classical PEM growth. Initially, with the addition of polycation, the PEM layer mass increases, indicating the sorption of the PDADMAC onto the layer. This increase is then quickly followed by a significant decrease in layer mass. The net result is a slight increase in layer mass after each PSBMA/PDADMAC bilayer adsorption. We reason that, due to the weak interactions of the PSBMA with the PDADMAC, quasi-soluble polyelectrolyte complexes (Q-PECs)⁴⁴ are formed during the addition of PDADMAC, which are washed away from the layer. This behavior is somewhat similar to the results of Sui et al, where similar odd even effects and a plateau in layer growth are seen for low molecular weight PEs.⁴⁵ Although the mechanism for the complex formation behind those results is fairly different, we think that, as in their case, for the PDADMAC/PSBMA layers the formation Q-PECs causes the desorption.

The above results show clear evidence of an interaction between PDADMAC and PSBMA at 0.5 M NaCl , which is in agreement with the results from Mary and Bendejacq.³⁸ In that work, the interactions of polyanions or polycations with different polyzwitterions were investigated, also demonstrating the same selective interactions between polycations and polyzwitterions, and no interactions between polyanions and polyzwitterions. As mentioned earlier, it has been proposed that the interactions of PDADMAC with PSBMA could be due to the presence of some negatively charged AA moieties that result from partial hydrolysis.³⁹ The hydrolysis will effectively result in a copolymer of PSBMA and PAA. To confirm the existence of specific SBMA-DADMAC

interactions, and exclude the possibility AA involvement, multilayers were built at pH 5.8, pH 3.4 and pH 2. If any AA monomers would be present, they would be dissociated at pH 5.8 and associated at pH 2.⁴⁶ From the work of Alonso et al.,⁴⁷ we know that the adsorbed amount per layer in PDADMAC/PAA multilayers strongly depends on the degree of dissociation of PAA. In our case however, lowering the pH from 5.8 to 2.0 hardly changed the observed layer growth. This is a strong indication that no AA monomers are present in our polymer and thus that specific interactions are present between PDADMAC and sulfobetaines groups.

As mentioned above, the growth of the PDADMAC/PSBMA multilayer seems to reach a plateau value. Furthermore, a clear odd-even effect is observed between the PDADMAC and PSBMA layers, with the observed stripping effect being typical for multilayers that are based on weak interactions.⁴⁵ This development of a maximum layer mass may limit the application of these systems, especially where thicker layers are needed. Changing the coating conditions, e.g. by changing the ionic strength or temperature, will yield a wider variety of layer thicknesses and thus more control on the membrane properties as will be discussed later.

Effect of the Ionic Strength on the Layer Buildup

The nature of polyelectrolytes in aqueous solutions is strongly dependent on the ionic strength.²⁸ Inter- and intrachain interactions of the zwitterions can be screened by ions in the medium. This changes the swelling degree, solubility, and critical solution temperatures of the polyelectrolytes. It is therefore interesting to examine the effect that this change in polyelectrolyte properties has on the growth of the zwitterionic multilayers. The first noticeable difference in the effect of the ionic strength is the stability of the layers during the coating. A clear difference in adsorption dynamics is found between growth at 0.5 M NaCl (Figure 2) and at lower salt concentrations (a representative result is shown for 0.2 M NaCl in Figure 3a). At lower concentrations, a relative stable PEM growth is shown, comparable to the behavior of classical PEMs, whereas at 0.5 M NaCl significant amounts of the PEM layer is rinsed away after initial adsorption. It can be expected that this loss of material due to the formation of Q-PECs (and thus the stability of the formed multilayers) is dependent on the salt concentration, something that is already known for classical polyelectrolyte complexes.⁴⁸⁻⁴⁹ It was also shown that for PDADMAC/PSBMA, the formation of complexes is dependent on the molar ratio of the two polymers, showing higher stabilities in the presence of a molar excess of one of the polymers.³⁸ In our case, at higher NaCl concentrations, more PSBMA and less PDADMAC are deposited on the wafer (Figure 3b), which will lead to a difference in the polymer ratio at the interface and thus in the stability of the multilayer. The higher solubility of the zwitterion, the change in PDADMAC/PSBMA ratios and an increase of extrinsic charge compensation (as will be discussed later) of the multilayer at higher ionic strength, will all favor the formation of the Q-PECs and result in the observed desorption at high ionic strengths.

The plateau adsorbed amounts, where no significant sorption occurs anymore, of the PDADMAC/PSBMA layer buildup is shown in Figure 3b for different concentrations of NaCl. In the Appendix of Chapter 5 the data of Figure 3b are supplied with different y-scale. A significant effect of the salt concentrations on the layer growth is found. For the first PDADMAC layer, the adsorption is somewhat larger at higher salt concentrations (from 0.4 mg·m⁻² at 0.005 M to 0.8 mg·m⁻² at 0.5 M NaCl), consistent with other work that investigated the role of ionic strength on the classical PEM growth.⁵⁰ However, for the whole polycation/polyzwitterion

Figure 3. A) Reflectometry graph from PDADMAC (+), background electrolyte solution (s) and PSBMA (z) in 0.2 M NaCl at pH 5.8. B) Effect of the ionic strength on the PDADMAC/PSBMA multilayer buildup (0.1 g·L⁻¹ polymer at pH 5.8).

system an increase in layer depositions at lower NaCl concentrations is found, the inverse of the classical polycation/polyanion systems. Additional reflectometry experiments at 1.0 M NaCl even showed no significant adsorption of PSBMA on a PDADMAC layer. The increase in layer mass at lower ionic strengths is mainly due to an increase in PSBMA deposition. A similar trend was found by Kato et al., who showed the effect of ionic strength on the adsorption of a single layer of polyelectrolyte on bare silica.⁵¹ They show a decrease in the polyelectrolyte adsorption between 0.06 and 2 M NaCl. The clear anomaly of the role that the ionic strength plays in the layer building further shows that interactions between the polycation and the zwitterionic moieties play a dominant role in this system.

It is known that zwitterionic polymers behave oppositely to polyelectrolytes with regards to their solubility and swelling at different ionic strengths.^{28, 52} Where the solubility of polyelectrolytes is decreased at higher salt concentrations, in the case of polyelectrolytes the solubility increases at higher salt concentrations - the so called anti-polyelectrolyte effect.^{28, 53} The solubility of polyelectrolytes, and subsequent chain coiling in solution, has been shown to influence the PEM growth. An increase in coiling of the polymer due to reduced electrostatic repulsions may result in rougher and thicker multilayers,^{16, 54} this is however found to be system dependent.⁵⁵ In the case of the zwitterionic polymers, due to the anti-polyelectrolyte effect, the coiling will be more prominent at low ionic strengths. This increase in coiling can lead to a higher roughness and thus the observed thicker layers at lower ionic strengths. For our layers however, rather smooth films are formed at 0.05 and 0.2 M NaCl ($R_a = 0.122$ and 0.170 nm respectively), while for the thin layer, prepared from 0.5 M NaCl, PEM islands are formed during the drying of the film with of roughness of 0.240 nm, comparable with results from Gui et al.³⁵ This indicates that an increase in layer roughness is not accompanied by thicker layer, rather the opposite is observed. Because of the zwitterionic nature of the PSBMA, unlike for classical PEs, little repulsion between the polymer chains will exist. In fact, there is significant attraction between the polymer chains at lower ionic strengths.²⁸ This lack of repulsion and the interchain interactions will result in smooth PSBMA layers as demonstrated here with AFM, even though polymer coiling may be present in solution.

Figure 4. Schematic representation of the counterion fate upon polyelectrolyte adsorption, depicting two extreme cases: TOP: At low ionic strength little to no counterions are present near the polyelectrolyte, and interpolymer interactions dominate. During adsorption, the counterions from the polycation will not be released, but shifted to the adsorbed polyelectrolyte. BOTTOM: At higher ionic strengths, counterions are present near the polyelectrolyte. Upon adsorption, these can be released to the solvent.

In classical polyanion/polycation multilayers, the change in the charge compensation at different ionic strengths determines the thickness of these multilayers.¹⁵ At low salt concentrations, the majority of the charges is compensated between the polyelectrolytes, so-called intrinsic charge compensation. At increasing ionic strengths, charge compensation by counterions is favored; thus, the equilibrium shifts to extrinsic charge compensation.¹⁵ A change in the charge compensation from intrinsic to extrinsic is accompanied by thicker and more mobile layers.^{15, 50} However, as the zwitterionic polymer is essentially charge neutral, the counterion release and charge compensation mechanisms are inherently different. A shift from intrinsic to extrinsic charge compensation with increasing ionic strength could still occur, but it does not seem to dominate the layer growth in our system. A proposed mechanism for our systems is shown in Figure 4, representing two cases: one for low ionic strengths and one for high ionic strengths.

At low ionic strength, little to no counterions are present in the coiled polyelectrolyte, and the intrachain interactions within the polymer chain dominate (Figure 4-TOP). As a result, there are relatively few anionic sites available in the polyelectrolyte for interaction with the positively charged substrate. Furthermore, there is hardly any counterion release upon polyelectrolyte adsorption. The few charges available and the low entropy gain will both favor the formation of thick polyelectrolyte layers. This can be seen in Figure 3b, where at 0.005 M NaCl for the first two layers, more than a tenfold of adsorbed PSBMA is observed compared to PDADMAC.

When increasing the ionic strength, more intramolecular interactions of the polyelectrolyte chain itself are screened by the mobile ions in solution, effectively supplying counterions for the polyelectrolyte. With this, more anionic species will also be available for interaction with the substrate, netting more free ionic moieties per polymer chain and thus thinner layers are formed. The formation of thinner films is also favored by the presence of the counterions in the polyelectrolyte. Upon adsorption to the polycation, the counterions that screen the intramolecular interactions of the polyelectrolyte can be released (see Figure 4-BOTTOM). This means that at higher ionic strengths the entropic gain of the adsorption is increased, which is known to result in thinner layers.¹⁵ This is supported by the results shown in Figure 3b, where the amount of PSBMA in the second layer reduces by an order of magnitude when increasing the NaCl concentration from 0.005 to 0.5 M NaCl. It must be noted that at increasing ionic strengths the net entropic gain of the counterion release will be reduced by the presence of more ions in the solution, just as is the case for all multilayers. The effect of ionic strength on the entropic gain of the polycation/polyelectrolyte will thus be opposite to the classical PE system, until the ionic strength reaches a point where counterion release hardly has any entropic gain. This strong -antipolyelectrolyte-like- effect of the ionic strength on the layer growth presented here shows that electrostatic interactions between PSBMA and PDADMAC and the coiling of the PSBMA play a dominant part in our multilayers. However, we do not exclude the presence of other phenomena (e.g., steric preference, hydrophobic interactions) between the polymers which might further increase the layer stability.

Polyelectrolyte Multilayer Assembly on PDADMAC/PSS Layers

The classical LbL technique is a versatile approach that can be used on a variety of surfaces. In order to test if this also applies for the case of our weak polyelectrolyte multilayers, PDADMAC/PSBMA multilayers were grown on a classical PDADMAC-PSS multilayer. The latter polyelectrolyte multilayer is a system that has been studied intensively.^{12-13, 56-57} As the PDADMAC/PSBMA multilayers either grow extremely rapid at low ionic strength or reach a plateau after a multitude of layers at higher ionic strengths, there is limited control on the layer thickness. This can be improved by combining the layer with PDADMAC/PSS layers. Even though the PDADMAC/PSBMA layer are expected to grow in a similar matter, the additional PDADMAC/PSS layer underneath will grant more control on the overall PEM thickness. The results of the dynamic reflectometry experiments are shown in Figure 5a, where initially 2 bilayers of PDADMAC (0.5 M NaCl) and PSS (0.5 M NaCl) are deposited on a silicon wafer, followed by 5 bilayers of PDADMAC (0.5 M NaCl) and PSBMA (0.5 M NaCl). The two bilayers of PDADMAC and PSS show the start of an exponential growth, typical for this PE combination at these NaCl concentrations.⁵⁶⁻⁵⁷ When switching to the polyelectrolyte system, the polymer film continues to grow, albeit significantly less per coating step. The growth of the PDADMAC/PSBMA multilayers behaves comparable to the growth on the bare silicon wafer as shown in

Figure 5. A) Reflectometry graph from multilayer assembly of PDADMAC/PSBMA layer on top of a (PDADMAC/PSS)₂ multilayer in 0.5 M NaCl at pH 5.8 (PDADMAC (+), PSS (-), PSBMA (z), electrolyte solutions (s)). B) Comparison of PDADMAC/PSBMA multilayers on top of a bare silicon wafer (▼) and on (PDADMAC/PSS)₂ (■), both in 0.5 M NaCl at pH 5.8.

the kinetic adsorption curve (Figures 2 and 5a): a significant increase of mass adsorption in the case of the PSBMA step, followed by partly washing away of this layer upon addition of PDADMAC. A comparison of the layer mass as measured with reflectometry on both a bare silicon wafer and on 2 bilayers of PDADMAC/PSS is given in Figure 5b. The results very much superimpose: the odd-even effect after multiple layers is apparent in both cases and the adsorbed amount per coating step is similar. These results show that the PDADMAC/PSBMA layers can easily be combined with conventional LbL systems, potentially bypassing limitations of the layer growth of the polyelectrolyte multilayers. Indeed, we believe that combining traditional and polyelectrolyte PEMs gives many additional possibilities to control the permeation behavior of PEM membranes.

Polyzwitterion Multilayer Assembly on Polymeric Hollow Fibers

Multilayers containing polyelectrolyte are coated on a polymeric hollow fiber membrane (Pentair X-Flow HFS) under the same conditions as on the silicon wafers. With a simple dip coating procedure as performed here, the polymer adsorption will predominantly be based on polymer diffusion, similar to the adsorption in the stagnation point flow cell used for the reflectometry measurements. The SPES present in the HFS provides a negatively charged surface (-25 mV in 5 mM KCl), making these membranes an appropriate substrate for polyelectrolyte multilayer growth. In Figure 6a, the effect of the salt concentration on the membrane resistance after each additional bilayer is shown. In all cases, the membrane resistance increases with the number of bilayers. Furthermore, the increase in resistance per coating step is highest at low ionic strength, where the reflectometry data show the largest layer growth. With increasing salt concentrations, less increase in membrane resistance is observed. As the resistance in membrane filtration through dense polymer films is linearly dependent on the layer thickness,⁵⁸ we can conclude that our model surface and membranes show identical trends with respect to the number coating steps and ionic strength dependence (see Figure 3b).

The zeta potential of the surface of the membranes was investigated after each coating step (Figure 6b). As expected, charge reversal of the negatively charged membrane was observed after coating with positively charged PDADMAC. However, upon addition of the PSBMA and subsequent PDADMAC/PSBMA multilayers, no charge reversal occurs and the membrane

Figure 6. $(\text{PDADMAC/PSBMA})_n$ polyelectrolyte multilayer grown on a hollow fiber membrane at pH 5.8 in 5 M NaCl. A) The effect of ionic strength of the coating solution on the membrane resistance. B) Membrane surface zeta-potential after each additional layer (measured at pH 7 in 5 mM KCl).

remains positive. This lack of charge reversal was also observed with poly(carboxybetaines) by Kharlampieva et al., although in their case the polyelectrolyte terminated layer was neutral.³¹ This lack of overcharging is due to the effective charge neutrality of the polyelectrolyte and explains the weak interactions and the growth to a plateau that was seen with our reflectometry measurements. With the absence of any charge reversal, the basic driving force of polyelectrolyte LbL assembly is missing. This could well explain why, in for example Figure 2, a plateau in the adsorbed amount was observed after 4 PSBMA layers.

Membranes were also coated in a similar fashion as the second multilayer systems discussed in the previous sections. First, 2 or 3 bilayers of PDADMAC/PSS from 0.5 M NaCl were coated on the membrane, followed by PDADMAC/PSBMA multilayers. The results are shown in Figure 7. Again, the data from the reflectometry correlate very well to the membrane resistance. The resistance per PDADMAC/PSBMA bilayer grows similar on top of PDADMAC/PSS

Figure 7. $(\text{PDADMAC/PSS})_m(\text{PDADMAC/PSBMA})_n$ polyelectrolyte multilayer grown on a hollow fiber membrane at pH 5.8 in 0.5 M NaCl. A) Membrane resistance after n amounts of PDADMAC/PSBMA multilayers on the bare HFS membrane and on the HFS membrane coated with either 2 or 3 bilayers of PDADMAC/PSS. B) Membrane surface zeta-potential after each additional layer for the $\text{HFs-(PDADMAC/PSS)}_2(\text{PDADMAC/PSBMA})_3$, measured at pH 7 in 5 mM KCl.

modified membranes as on the bare HFS membranes. However, the final membrane resistance after a total of 5 bilayers does differ, depending on the amount of PDADMAC/PSS layers that are coated initially. The membrane zeta-potential results for the $(\text{PDADMAC/PSS})_2/(\text{PDADMAC/PSBMA})_n$ systems are comparable to the PDADMAC/PSBMA systems (Figures 6b and 7b). Initially, the membrane charge is reversed by alternating between polyanion and polycation terminated layers in the membrane, according to expectations.⁵⁶ After the addition of PDADMAC/PSBMA layers, the membrane zeta-potential remains positive. These results show that by combining the PDADMAC/PSS multilayers with the zwitterionic multilayers, the resulting membrane properties can be very well controlled. For instance, the plateau adsorbed amount for the zwitterionic multilayer growth that was found with reflectometry will also occur on the membrane surface. This will limit the final resistance of the membrane that can be obtained and is undesirable for applications where thicker and denser membranes are needed to allow separation between water and small solutes (e.g., desalination). This can be circumvented by coating the membrane initially with the classical multilayers that show a linear growth profile and terminating with the zwitterionic multilayers.

Figure 8. Ionic strength responsive behavior of $(\text{PDADMAC/PSS})_2$ (▼, ▽), $(\text{PDADMAC/PSS})_2-(\text{PDADMAC/PSBMA})_1$ (■) and $(\text{PDADMAC/PSBMA})_5$ (●) modified HFS membranes.

We have shown that the membrane resistance, and thus permeability, is predominantly controlled by the amount of polymer that is adsorbed on the membrane surface. With each additional layer, the resistance of the membrane increases. Also, the incremental resistance per layer is higher at lower salt concentration, where the layer buildup is higher. All these resistances are determined for the filtration of pure water. Figure 8 presents the permeability data for filtration at different NaCl concentration and shows that the permeability is also dependent on the ionic strength of the filtration solution. For these experiments, membranes with little to no retention of NaCl were chosen. As such, we avoid any concentration polarization and osmotic pressure differences during the filtration, which both can influence the flux through the membrane.⁵⁸ A responsive behavior of the membrane with 5 bilayers of PDADMAC/PSBMA coated from 0.5 M NaCl is found, showing an increase in permeability of 41% from 0 to 1.5 M NaCl. To assess if the increase in permeability is not due to a loss of the multilayer, the pure water permeabilities are measured again after each filtration with the different NaCl solutions. Only slight changes in the pure water permeability that are within the standard error of the measurement (<10%) are observed for the fiber treated up to 1.5 M NaCl. As such, removal of (part of) the layers did not

occur during the filtration with salt solutions. For a membrane with 2 bilayers of PDADMAC/PSS and 1 bilayer of PDADMAC/PSBMA coated at 0.5 M NaCl again a responsive behavior toward the ionic strength is observed. This membrane is even more responsive as compared to the PDADMAC/PSBMA₅ membrane, with an increase in permeability of 108% from 0 to 1.5 M NaCl. As is the case for the other membrane, no loss of the multilayer was observed, indicated by the stable pure water permeability. For comparison, in Figure 8 the responsive behavior of a membrane coated with just (PDADMAC/PSS)₂ that is exposed to different NaCl solutions, is also shown. Up to 1.0 M NaCl, the permeability of the membrane does not change significantly, in both electrolyte solutions as in pure water. At 1.5 M, the permeability increases by 22%. This change in permeability is however irreversible (indicated in Figure 8 by the open symbol), as shown by the pure water permeability after 1.5 M NaCl treatment, which increased as well from 24 to 32 L·m⁻²·h⁻¹·b⁻¹. This change, as observed by Han et al. for PDADMAC/PSS multilayers above 1.0 M NaCl, is attributed to a rearrangement of the PEM.²⁶ This irreversible change of the pure water permeability does not constitute as stimuli responsive behavior of the membrane. As shown in Figure 8, the addition of a PDADMAC/PSBMA bilayer on top of the (PDADMAC/PSS)₂ multilayer notably changes the properties of the whole multilayer. Not only is the layer responsive to the ionic strength, the layer is also found to be stable above 1 M NaCl. This indicates that no discrete layers are formed, but the PSBMA interpenetrates the whole of the layer. This is a rational conclusion, attributed to the known interpenetration of the different layers⁹, which was recently shown to occur for 12-14 layers in the case of PDADMAC/PSS at 0.5 M NaCl.⁵⁹ Our results clearly show that, by incorporating zwitterionic polymers, ionic strength responsive membranes are obtained. Creating these responsive membranes is very easily done, in just a few simple and flexible dip-coating steps, which gives excellent control on the membrane properties.

It is interesting to remark that the type of observed responsive behavior also gives information on the location of the multilayer on the membrane. For multilayers, one can always question if the coating procedure leads to a multilayer on top of the membrane or a coating of the pores inside of the membrane. The ionic strength responsive behavior shown here is a clear indication that a dense film is coated on top of the membrane. Upon increasing the ionic strength, a polyelectrolyte film will swell more due to anti-polyelectrolyte effect.⁵² A more swollen polymer film will have an increase in solute transport,⁶⁰ in our case manifested by an increase in permeability at higher ionic strength. This response is opposite to membranes that have polyelectrolyte films coated on the inside of the pores. In that case an increase in swelling will close the pore and will thus result in a lower permeabilities.³⁰ The membranes with a dense zwitterionic film presented here can be of interest in applications where ionic strength responsive behavior is wanted in combination with small solutes (e.g., trace ions or low molecular weight organics separations), where separations based on pure size exclusion through pores will not suffice and charge and affinity also play a large role. For those systems, the ionic strength can function as an optimization parameter to obtain the best possible membrane performance.

5.4 Conclusion

We show here that the strong polyelectrolyte PSBMA, combined with the cationic PDADMAC, can be used to make zwitterionic multilayers via the LbL technique on different surfaces. The growth of the layers is found to be independent of the substrate used. Coating on either bare

silicon wafers, on (PDADMAC/PSS)_n layers, on hollow fiber membranes or on membranes precoated with (PDADMAC/PSS)_n yields similar results for all systems. The ionic strength during depositing is found to be a parameter that strongly influences the layer growth. Stable multilayer growth is observed at lower NaCl concentrations, while at 0.5 M NaCl part of the layer are washed away during additional coating steps. We explain that, although the PSBMA is essentially charge neutral, counterion release during polymer adsorption can play a part in the layer growth. Opposite to classical LbL systems, increasing the ionic strength results in thinner layers, which is attributed to the zwitterionic nature of the PSBMA. In our systems no effect of pH is observed on the layer growth, as expected for the combination of a strong polyelectrolyte with a strong polycation.

Zwitterionic systems have several unique features that make them interesting materials for different applications. A notable property is the interaction of the polyelectrolyte with electrolytes, the “anti-polyelectrolyte effect”, which can be used to make surfaces stimuli responsive. In our case, the ionic strength is shown to reversibly change the hollow fiber membrane performance. We show this by the ionic strength responsive behavior of the membranes modified with the zwitterionic layers. An increase in membrane permeability, of even more than 100% at 1.5 M NaCl, is observed and can be explained by increased swelling of the zwitterionic layers with increasing salt concentrations.

The approach used in this chapter, combining reflectometry results on model surfaces with macroscopic characterization of membranes coated with similar layers, proves to be valuable in understanding the behavior of the LbL systems. Our results from both the reflectometry measurements and the membrane performance are not only in agreement with each other but are supplementary as well. From reflectometry we get a good understanding of the amount of polymer in the multilayer and of its stability, while permeation experiments provide an indication of how open/swollen the layer is.

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Appendix Chapter 5

HFS Membrane Structure

Scanning electron microscope (SEM) pictures made with a JEOL JSM-5600LV are presented in Figure 9, showing the asymmetric spongy structure of the used HFS membrane. The membrane has a tight SPES layer on the lumen side, while to outside of the membrane has an open porous structure.

Figure 9. SEM images of the HFS membrane used in this study: A) cross-section of the hollow fiber $\times 500$; B) Inner membrane surface $\times 40,000$; C) Outer membrane surface $\times 10,000$.

^1H -NMR Analysis of PSBMA

The PSBMA was analyzed by means of ^1H -NMR in D_2O with 0.2% M NaCl on a Bruker Ascend 400 MHz. The spectrum is shown in Figure 10. All peaks in the spectrum can be ascribed to the proton of the neat PSBMA (δ 1.0 (3H), 1.2-2.2 (2H), 2.3 (2H), 3.0 (2H), 3.3 (6H), 3.6 (2H), 3.8 (2H), 4.5 (2H)).⁶¹ Additionally, the lack of any signal at 10-12 ppm further shows that no acrylic acid moieties are present. This indicates that no significant hydrolysis takes place during the PSBMA synthesis.

Figure 10. ^1H -NMR spectra of the synthesized PSBMA. The peak at 4.7 represents the D_2O solvent.

Atomic Force Microscopy Imaging of Dry PDADMAC/PSBMA₁ Films

To support our theoretical Q-factor used for the reflectometry measurements, we also measured the thickness and roughness of some dry layers by atomic force microscopy (AFM). Tapping mode AFM analysis was carried out with a Dimension D3100 atomic force microscope equipped with a hybrid scanner and a NanoScope IVa controller (Veeco/Digital Instruments (DI), Santa Barbara, CA, USA) using PointProbe® Plus silicon probes (PPP NCH, Nanosensors, Neuchatel, Switzerland) in ambient conditions. The system operating frequency was typically 15% lower than the natural resonance frequency of the cantilever in air, the free amplitude was kept constant, while the set point amplitude was approximately 80 % of the free amplitude (~ 1.5 V). For the roughness, the arithmetic average of the absolute values of the surface heights deviations was taken (R_a). Bilayers of PDADMAC/PSBMA was applied on a SiO₂ wafer via dip-coating in 0.1 g·L⁻¹ polymer solutions in either 0.05, 0.2 or 0.5 M NaCl. The thickness of the bilayers were measured via the scratch technique. The thicknesses of PDADMAC/PSBMA bilayers grown on a silicon wafer are 5.5, 3.5 and 1.6 nm for 0.05, 0.2 and 0.5 M NaCl. In Figure 11, the surface morphologies from PDADMAC/PSBMA₁ coated at different ionic strength are shown. At 0.05 and 0.2 M NaCl rather smooth layers are formed ($R_a = 0.122$ and 0.170 nm respectively). At 0.5, the dry layer shows PEM islands, similar to results from Gui et al.³⁵ Layers coated at 0.5 M NaCl have a roughness of $R_a = 0.240$.

Figure 11. AFM images of PDADMAC/PSBMA bilayers coated at 0.05, 0.2 and 0.5 M NaCl.

Effect of the Ionic Strength on the PDADMAC/PSBMA Multilayer Growth.

The growth of the PDADMAC/PSBMA multilayer at low ionic strength ($0.1 \text{ g}\cdot\text{L}^{-1}$ polymer at pH 5.8), is shown in Figure 12 in more detail. The growth is characterized by a very rapid increase in layer mass already after a few multilayers. It must be noted that the final points of each data set in Figure 12 is the minimum adsorption value on the wafer of these layers. In reflectometry, linearity of the data is only maintained for a layer thickness between 60-150 nm.⁴⁰ For these specific layers, the experimental data clearly showed a deviation from this linearity. As a results no accurate values for the adsorption mass can be given, and the value at which the deviation from linearity was observed is chosen.

Figure 12. Effect of the ionic strength on the PDADMAC/PSBMA multilayer buildup ($0.1 \text{ g}\cdot\text{L}^{-1}$ polymer at pH 5.8).

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*Charged Micropollutant Removal With Hollow Fiber Nanofiltration Membranes Based On
Polycation/Polyzwitterion/Polyanion Multilayers*

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Zwitterionic Polyelectrolyte Multilayers For Nanofiltration Membranes

Abstract

Hollow fiber nanofiltration membranes can withstand much higher foulant concentrations than their spiral wound counterparts and can be used in water purification without pretreatment. Still, the preparation of hollow fiber nanofiltration membranes is much less established. In this chapter, we demonstrate the design of a hollow fiber nanofiltration membrane with excellent rejection properties by alternatively coating a porous ultrafiltration membrane with a polycation, a polyzwitterion and a polyanion. On model surfaces, we show, for the first time, that the polyzwitterion poly N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (PSBMA) can be incorporated into traditional polyelectrolyte multilayers based on poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC). Furthermore, work on model surfaces allows a good characterization of, and insight into, the layer build-up and helps to establish the optimal membrane coating conditions. Membranes coated with these multilayers have high salt rejection of up to 42% NaCl, 72% CaCl₂ and 98% Na₂SO₄ with permeabilities of 3.7 - 4.5 L·m⁻²·h⁻¹·bar⁻¹. In addition to the salt rejections, the rejection of six distinctively different micropollutants, with molecular weights between 215 and 362 g·mol⁻¹, was investigated. Depending on the terminating layer, the incorporation of the polyzwitterion in the multilayer results in nanofiltration membranes that show excellent retentions for both positively and negatively charged micropollutants, a behavior that is attributed to dielectric exclusion of the solutes. Our approach of combining model surfaces with membrane performance measurements provides unique insights into the properties of polyzwitterion-containing multilayers and their applications.

6.1 Introduction

The intensification of the use and reuse of freshwater resources comes at a cost. Reports on rising levels of emerging contaminants in our water are numerous.¹⁻⁴ And with the world population growing in number, age, and level of welfare, the strain that these newborn contaminants puts on drinking water will only increase. After the successful development of treatment methods based on porous membranes (e.g., ultrafiltration (UF)) that are designed to remove harmful yet mainly macroscopic sized contaminants such as bacteria, cryptosporidium, and viruses, the development of the next generation membranes for water treatment is essential. The main focus will lie on the removal of small organic contaminants that are typically harmful after prolonged exposure to low concentrations.³ These emerging contaminants, also called micropollutants (MPs), are industrial, medicinal and agricultural wastes such as nonylphenols, sulfamethoxazole, atenolol and atrazine.^{3,5} They are characteristically small, with molecular weights ranging between 100 and 1,000 Da, and have the potential to cause long-term harm to humans and the environment. Because of their small size, conventional membrane filtration with relatively large pores, such as UF and microfiltration (MF), is not sufficient for their removal.

Using nanofiltration (NF) membranes have been proposed as a cost-effective method to remove micropollutants.⁶ Numerous studies have shown that commercially available NF membranes are capable to retain several contaminants, but that the rejection depends on the properties of the micropollutant.⁷⁻¹⁵ Although the rejections of NF membranes are significantly lower compared to those of reverse osmosis (RO), it is argued that this drawback can be overcome by an appropriate post-treatment.⁶ All commercially available NF membranes (e.g., NF270 & NF90 from DOW, ESNA from Hydranautics, TFC-SR3 from Koch) are flat sheet membranes in a spiral wound module, which have limited hydraulic and chemical cleaning possibilities. This means that in addition to the optional post-treatment, an extensive pre-treatment (e.g., UF or rapid sand filtration) of the feed is required in order to reduce (bio)fouling on the spacers and the membrane.^{16,17} The pretreatment comes with additional operational costs,¹⁸ and a significant cost saving can thus be obtained if this pretreatment could be skipped by using hollow fiber NF membranes instead of spiral wound NF membranes (see Figure 1).¹⁹ Just as is the case for hollow fiber UF membranes, hollow fiber NF membranes are able to withstand much higher foulant concentrations without any detrimental effects such as spacer clogging. Unfortunately, commercial hollow fiber NF membranes for these applications are scarce, with the only choice at the moment being Pentair X-Flow's HFW 1000 membrane with a relatively high molecular weight cut-off of approximately 1,000 Da. This means that there is a strong need for the development of hollow fiber membranes with dense NF filtration properties.

Several methods have been investigated to obtain hollow fiber membranes with NF-like properties. Thin polyamide layers have been applied on hollow fibers via interfacial polymerization, an approach very similar to that of the thin film composite (TFC) spiral wound membranes.²⁰ However, these TFC composite polyamide layers are easily degraded in the presence of oxidizing agents. This significantly limits the possibilities to remove (bio)fouling from the membrane, e.g., via oxidation with hypochlorite, as this would harm the performance of the membrane over time.²¹ Additionally, due to the lack of pretreatment, the hollow fiber NF feed will have a much higher foulant load that will require a NF layer designed to cope with this. We therefore argue that successful hollow fiber NF membranes should either be stable against hypochlorite degradation and/or have good antifouling properties. For chemically stable NF membranes, dense layers of

Figure 1. Flow scheme of (left) a traditional spiral wound NF process with an additional pretreatment for the feed and (right) of the proposed direct hollow fiber NF process without pretreatment.

sulfonated poly(ether ether ketone) (SPEEK) are coated, typically on top of poly(ether sulfone) (PES) supports.²² Jung et al. applied a thin layer of SPEEK on hollow fiber UF membranes to remove aromatic pesticides,²³ while in a comparable way, SPEEK was used by Song et al. to remove glyphosate.²⁴ Recently, a more facile method for membrane modification based on the self-assembly of oppositely charged polyelectrolytes has received increased attention.²⁵⁻²⁷ In this so-called layer-by-layer (LbL) assembly, a substrate is alternatively exposed to polycations and polyanions to build polyelectrolyte multilayers (PEMs) of controllable thickness.²⁸ The versatility of this approach allows the PEMs to be grown on a multitude of substrates, thus enabling its use for the development of hollow fiber NF.^{29, 30} By choosing chemically stable polyelectrolytes, dense thin layers that have increased chemical cleaning possibilities or low fouling resistance can be obtained. In addition to polycations and polyanions, other (multi)functional macromolecules can be incorporated into the multilayer, leading to enhanced properties of the layers.^{31, 32, 33, 34} An example of these macromolecules are polyelectrolytes, polymers that contain both positive and negative moieties on the same monomer. Polyelectrolytes exhibit unique properties which make them interesting materials for a variety of applications, such as low-fouling coatings, sensors and chromatography.^{35, 36} Moreover, NF membranes with grafted zwitterionic moieties have been shown to have improved rejections and improved antifouling properties.^{37, 38} For LbL systems, it was shown by Kharlampieva et al. that under acidic conditions, weak polyelectrolytes can be incorporated into traditional multilayers.³¹ In a previous study we showed that the site specific interactions between a strong polyelectrolyte and a polycation can also be used to grow zwitterionic multilayers for stimuli responsive membranes without the need for acidic conditions.³⁹

In this chapter we employ the LbL concept using zwitterionic polymers for the development of the next generation hollow fiber NF membranes and show that the retention behavior of these membranes for emerging contaminants can be tailored depending on the intrinsic properties of the applied layers. We report, for the first time, on the incorporation of the polyelectrolyte poly N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (PSBMA) in LbL assembled multilayers of poly(diallyldimethylammonium chloride) (PDADMAC), a strong polycation, and poly(styrenesulfonate) (PSS), a strong polyanion. Trilayers of PDADMAC/

Figure 2. Schematic representation of the coating of a charged hollow fiber membrane with a trilayer of PDADMAC (+), PSBMA (z) and PSS (-) on a charged hollow fiber membrane.

PSBMA/PSS are formed. The effect of ionic strength on the trilayer assembly on silicon wafers as model surfaces is investigated to understand the layer growth. Similar layers are then coated on charged polymeric membranes to make hollow fiber NF membranes (see Figure 2), which are characterized by means of water permeability and ion and micropollutant rejection. Finally, the fundamental insights of the layer growth obtained from model surfaces are correlated to the permeability and rejection behavior of the developed hollow fiber NF membranes.

6.2 Experimental

Materials

An aqueous solution of 20 wt% polydiallyldimethylammonium chloride (PDADMAC, Mw = 150 kDa) was obtained from Kemira (Finland). An aqueous solution of 20 wt% polystyrene sulfonic acid (PSS, Mw = 100 kDa) was obtained from Tosoh Organic Chemical Co., LTD (Japan). N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA) was obtained from Sigma Aldrich (The Netherlands) and used for polymerization without any further purification steps. The PSBMA was synthesized via an aqueous radical polymerization of SBMA with sodium peroxodisulfate at 70 °C and has a molecular weight of 500 kDa. The PSBMA synthesis and characterization is described in more detail elsewhere.³⁹ All other chemicals were purchased from Sigma Aldrich (The Netherlands).

Reflectometry

The multilayer growth on silicon wafers was monitored by means of reflectometry.⁴⁰ For this, 0.1 g·L⁻¹ cationic, zwitterionic, and anionic polymer solutions with the appropriate ionic strength were prepared and alternatively adsorbed onto a silicon wafer with a 75 nm SiO₂ top layer. The use of a stagnation point flow cell allows for very well controlled hydrodynamics during the multilayer growth. Polarized monochromatic light (He-Ne laser, 632.8 nm) hits the wafer around the Brewster angle and is reflected toward the detector. The reflected light is split into its p- and s- polarized components. The ratio between these two components is defined as S (-) and the change in this ratio (ΔS) is directly proportional to the amount of mass adsorbed on the wafer, according to equation 1:

$$\Gamma = \frac{\Delta S}{S_0} Q \quad (1)$$

where Γ is the amount of mass adsorbed on the wafer (mg·m⁻²), S_0 is the starting output signal

of the bare silicon wafer (-), and Q is the sensitivity factor for the system ($\text{mg}\cdot\text{m}^{-2}$). To calculate the sensitivity factor, we used an optical model based on the following values: $q = 71^\circ$, $n_{\text{silica}} = 1.46$, $\bar{n}_{\text{silicon}} = (3.85, 0.02)$, $n_{\text{H}_2\text{O}} = 1.33$, $\text{dn}/\text{dc}_{\text{PDADMAC}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, $\text{dn}/\text{dc}_{\text{PSBMA}} = 0.14 \text{ mL}\cdot\text{g}^{-1}$, $\text{dn}/\text{dc}_{\text{PSS}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, $d_{\text{silica}} = 75 \text{ nm}$.^{39, 41} The sensitivity factor (Q) obtained to calculate the actual mass adsorption for all experiments is $30 \text{ mg}\cdot\text{m}^{-2}$, a value that was validated by atomic force microscopy measurements for similar layers in our previous work.³⁹

Contact Angle

Optical contact angle measurements were performed on an OCA15 plus from Dataphysics Instruments. For this, silicon wafers were dip-coated for 20 min in $0.1 \text{ g}\cdot\text{L}^{-1}$ cationic, zwitterionic or anionic polymer solutions with 0.2 M NaCl in an alternating fashion. After each single polymer addition, the coated wafers were rinsed with a background electrolyte solution of 0.2 M NaCl for 20 min. The contact angle of the sessile drop of 2 ml water on the appropriate LbL coating was measured five times for each coating at 22°C , and the average and standard deviation are reported. The contact angles were measured five seconds after the bubble was placed on the surface.

Membrane Modification and Characterization

Polyelectrolyte multilayers were coated on dense ultrafiltration membranes prepared from sulfonated poly(ether sulfone) (Hollow Fiber Silica (HFS), kindly provided by Pentair X-Flow (The Netherlands)). These are hollow fiber membranes with a molecular weight cutoff of 10 kDa. Before the coating of the membranes, we first wetted the fibers overnight in a 15 wt% ethanol solution in water and rinsed them with demineralized water. The membranes were coated via a simple dip-coating procedure. For the trilayer coatings, the fibers were completely immersed in a $0.1 \text{ g}\cdot\text{L}^{-1}$ polycation solution with 0.2 M NaCl at room temperature. After 30 minutes, the fibers were subsequently rinsed in three separate solutions containing only NaCl with an ionic strength similar to that of the coating solution for 10 min in each solution, after which a membrane sample was taken. The remaining samples were subsequently dipped for 30 minutes in an alternating fashion in PSBMA, PSS and PDADMAC solutions with 0.2 M NaCl , taking a membrane sample after each coating step. After being rinsed, all membrane samples were put in a glycerol/water (15 / 85 wt%) mixture for 4 hours and dried overnight under ambient conditions. For the filtration experiments, single PEM coated membrane fibers were potted in a module with a fiber length of approximately 200 mm.

The water permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) was calculated by normalizing the measured pure water flux with the trans membrane pressure. The pure water flux was measured at 20°C with demineralized water in dead-end mode at a trans-membrane pressure of 2 bar. The membrane permeability was measured for two separate coating experiments, each in duplicate. The average of the permeability and the standard deviation is reported. For the salt retention measurements, a cross-flow through the fibers was applied. To limit the effect of concentration polarization, the cross-flow velocity of the feed through the fibers was set at $4.6 \text{ m}\cdot\text{s}^{-1}$. This corresponds to a Reynolds number of approximately 3,500, well above the transition to turbulent flow. The salt concentrations of the retentate and permeate were measured with a WTW Cond 3210 conductivity meter. The retention was based on the ratio between the permeate and concentrate concentrations.

The zeta potential of the membranes was determined with a SurPASS electrokinetic analyzer (Anton Paar, Graz Austria). The zeta potential was calculated by measuring the streaming current versus the pressure in a 5 mM KCl solution (pH 5.8) at room temperature, using the following equation:

$$\zeta = \frac{dI}{dP} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \kappa_B \cdot R \quad (2)$$

where ζ is de zeta potential (V), I is the streaming current (A), P is the pressure (Pa), η is the dynamic viscosity of the electrolyte solution (Pa·s), ε is the dielectric constant of the electrolyte (-), ε_0 is the vacuum permittivity (F m⁻¹), κ_B is the bulk electrolyte conductivity (S·m⁻¹), and R is the electrical resistance (Ω) inside the streaming channel. For each point, the zeta-potential is measured four times for two different membranes and the average and standard deviation is reported.

Micropollutant Analysis

For the characterization of the NF membranes, a selection of six common micropollutants (Figure 3) has been made for rejection experiments. The micropollutant molecular weight range is between 200 and 400 g·mol⁻¹, in the order of the typical molecular weight cutoff (MWCO) of NF membranes. The selection is made such that it covers neutral, positive and negative molecules at the measurement pH of 5.8 and contains both hydrophobic and hydrophilic molecules (Table 1). This ensures that the role of the solute charge can be properly assessed. Solutions containing all six micropollutants at a concentration of 10 mg·L⁻¹ each were filtered through the prepared membranes for at least 24 hours before collecting the permeate sample. This filtration time is needed to ensure steady state rejections. In order to reduce concentration polarization, a cross-flow velocity of around 4.6 m·s⁻¹ was applied. The trans-membrane pressure during filtration was 1.75 bar. Micropollutant rejections were calculated based on the differences between permeate and concentrate concentrations. The micropollutant concentrations in the feed and permeate were determined via liquid chromatography. For this, a Dionex Ultimate 3000 U-HPLC system equipped with a RS variable wavelength detector was used. Micropollutant separation was done on an Acclaim RSLC C18 2.2 mm column (Thermo Scientific) at 65 °C, while applying a gradient flow from 95 wt% H₂O + 5 wt% acetonitrile at pH 4 to 5 wt% H₂O + 95 wt% acetonitrile at 1 mL·min⁻¹.

Figure 3. Chemical structures of the six micropollutants selected for this chapter.

Table 1: Properties of the six micropollutants selected for this chapter; chemicalize.org by ChemAxon was used for generating the structure property prediction (<http://www.chemicalize.org>).

	pKa (-)	LogP (-)	Mw (g·mol ⁻¹)	Charge (at pH 5.8)
Atenolol	9.7	0.43	266.33	+
SMX	2.0/7.7	0.79	253.28	0
Atrazine	3.2	2.20	215.68	0
Bisphenol A	10.1	4.04	228.29	0
Naproxen	4.2	2.99	230.26	-
Bezafibrate	3.8	3.99	361.819	-

6.3 Results and Discussion

Multilayer Growth

The multilayer growth on silicon wafers is monitored in-situ with reflectometry. A silicon wafer is exposed to 0.1 g·L⁻¹ solutions of PDADMAC (+), PSBMA (z) and PSS (-) until a stable plateau in the adsorbance is obtained. All solutions contain a background electrolyte, and the different polyelectrolytes are coated in an alternating fashion as shown in Figure 4. Before switching to a different polyelectrolyte solution, the measurement cell is always rinsed with the appropriate background electrolyte solutions for at least 100 seconds, to prevent any possible bulk association of polyelectrolytes. The results of the multilayer growth at different ionic strengths is shown in Figure 4, where the polyelectrolyte adsorption in mg·m⁻² is plotted as a function of time.

Figure 4 clearly shows, for the first time, the possibility of the formation of PDADMAC/PSBMA/PSS trilayers on a silicon wafer. The results also show a significant dependence of the multilayer growth on the ionic strength. For pure polycation/polyanion multilayers it is well-known that the layer thickness or adsorbed mass increases with increasing ionic strength. This is explained by a shift in the polyelectrolyte charge compensation from intrinsic to extrinsic at higher ionic strengths, which is accompanied by thicker, more open and mobile layers.^{42, 43} In contrast to this, for multilayers based on a polycation and a polyzwitterion, we showed recently that the layer mass dependence on the ionic strength behaves opposite: a decrease in layer mass is observed at higher ionic strength, which is predominantly attributed to the higher solubility of the zwitterion at higher ionic strengths, the so-called anti-polyelectrolyte effect.^{39, 44} Figure 4 shows that for the PDADMAC/PSBMA/PSS trilayers the influence of this anti-polyelectrolyte effect is also present. At the lowest ionic strength the highest adsorbances are found, which is caused by the especially high adsorption of the polyzwitterion. With increasing ionic strength, the adsorption of PSBMA per coating step decreases. The decrease of PSBMA adsorption at higher ionic strengths also results in that at 1.0 M almost no significant PSBMA adsorption is observed. This means that at 1.0 M NaCl, we effectively observe the formation of almost pure

Figure 4. Typical reflectometry graphs showing the subsequent adsorption of PDADMAC (+), PSBMA (z), and PSS (-) from (top left) 0.05, (top right) 0.1, (bottom left) 0.2 M and (bottom right) 1.0 M NaCl solutions. Note the different y-axis scales for each graph.

PSS/PDADMAC bilayers. In parallel with the reduction of the PSBMA adsorption when coating at higher ionic strengths, the PDADMAC and PSS adsorption increases at higher ionic strength. This is a classical PEM behavior, caused by the shift to extrinsic charge compensation.⁴³ However, as the decrease in PSBMA adsorption is more pronounced, the net result is an overall decrease of the multilayer mass per trilayer at higher ionic strengths.

In addition to the changes of the layer masses adsorbed at different ionic strength, the adsorption kinetics also change as function of the ionic strength. At 0.05 and 0.1 M, initially, an excess of PSBMA is adsorbed, which is then slowly rinsed away during the measurement. At 0.2 M NaCl a stable layer growth is observed, comparable to growth of classical PEMs.⁴² Similar observations in dynamics during the coating of polycation/polyzwitterion multilayers at different ionic strengths were previously observed,³⁹ attributed to solubility changes and concentration dependence of the nature of the formed PDADMAC/PSBMA complexes.⁴⁵ We reason that similar changes in the solubility of the different complexes of the PDADMAC, PSBMA, and PSS can be attributed to the different growth dynamics observed here. Furthermore, at 0.2 M NaCl the amount of polymer adsorbed per layer is similar for all three polyelectrolytes. Because of this even distribution between the three different polyelectrolytes at 0.2 M NaCl and the fact that this concentration shows the most stable layer growth, further experiments are performed with trilayers grown at 0.2 M NaCl.

The wettability of the multilayers coated from 0.2 M NaCl was investigated for different terminating layers by means of contact angle measurements. The contact angle measurements give insight into the hydrophilicity of the layers, which is especially important for water

filtration applications. As expected, the results presented in Table 2, show a change of the layer hydrophilicity for differently terminating layers. The high contact angle obtained for PSBMA terminated layers is a result of the anti-polyelectrolyte effect: in pure water, the zwitterionic polymer has a hydrophobic nature due to the high interchain interactions of the zwitterionic charges.⁴⁴ Both the PDADMAC and PSS terminated layers are more hydrophilic as compared to the zwitterionic terminated layers. When comparing only the two polyelectrolytes, the lowest contact angle is observed for PSS terminated layers, which is comparable to what was found for pure PDADMAC/PSS bilayers.⁴⁶

Table 2: Trilayer contact angle measurements on silicon wafers for different terminating layers.

Layer	Contact Angle (°)
(PDADMAC/PSBMA/PSS) ₁ -PDADMAC (+)	55.9 ± 11.4
(PDADMAC/PSBMA/PSS) ₁ -PDADMAC/PSBMA (z)	72.5 ± 7.1
(PDADMAC/PSBMA/PSS) ₂ (-)	32.1 ± 4.0

Polymeric Hollow Fiber Membrane Modification

Polymeric hollow fiber membranes (HFS membranes from Pentair X-Flow) were coated with the polyelectrolyte trilayers from solutions containing 0.2 M NaCl. After each coating step, a membrane sample was taken for permeability and zeta-potential measurements. The results in Figure 5 show the successful trilayer growth on the membrane. With the addition of more polyelectrolyte trilayers on the membrane, the permeability significantly decreases, especially after the first layers. After each PDADMAC and PSBMA addition the permeability decreases, which is a clear indication of polymer adsorption. However, with each PSS addition, the permeability increases again. Our reflectometry results show that this increase in permeability cannot be caused by material removal during the PSS step, because no layer loss is observed

Figure 5. HFS membrane modification with trilayers of PDADMAC (+), PSBMA (z) and PSS (-) from 0.2 M NaCl: A) HFS-modified membrane permeability (L·m⁻²·h⁻¹·bar⁻¹) after each additional layer. B) Membrane zeta-potential (mV) after each coating step, measured in 5 mM KCl at pH 5.8. For all points, the error bars indicate the standard deviation.

while coating from 0.2 M NaCl (Figure 4). This means that a PSS terminated layer is itself more permeable to water, even though in total more polymer is adsorbed on the membrane. Such increases in permeability after an additional coating can be attributed to an changes in water affinity of the different terminating layers.^{47,48} Our contact angle measurements of the multilayers indeed show the lowest contact angle for the PSS terminated layer, supporting that the increase in the membrane permeability is caused by the higher hydrophilicity of the PSS terminated layers.

Next to an understanding of the membrane permeability, the membrane zeta-potential measurements after each additional layer provide insight into the formation of the trilayers on the fiber. As shown in Figure 5B, complete charge reversal of the negative membrane surface occurs when a PDADMAC layer is applied. The subsequent coating of the essentially neutral PSBMA results in a slightly lower yet still positive membrane. The absence of charge reversal is explained by the charge neutrality of the polyzwitterion and was also observed for membranes coated with PDADMAC/PSBMA bilayers.³⁹ Charge reversal is again obtained when the PSBMA-terminated layer is coated with PSS, resulting in a negatively charged membrane. This charge reversal after the PSS addition also confirms the adsorption of PSS on the membrane. For each additional trilayer, the same behavior of charge reversal by the addition of only PDADMAC and PSS is observed. These results on the hollow fiber membrane, which are in good agreement with the experiments on model surfaces, show the possibility of incorporating a zwitterionic polymer into a polyanion and polycation-based PEM, both on model surfaces and on porous membranes.

Polymeric Hollow Fiber Membrane Performance

The performance of our membranes coated with different layers is determined by their ability to retain different solutes. To study this, membranes were taken that were coated with 7, 8, or 9 monolayers, and which were thus terminated with either PDADMAC (+), PSBMA (z) or PSS(-). This provides insight into the effect of the terminating layer. NF membranes are typically characterized by their ability to retain different salts.⁴⁹ Several models have been developed to describe the rejections of ions, taking size, charge, valence and dielectric exclusion into account.^{49, 50, 51} A characteristic dependence on the ion valence is typical for Donnan exclusion, while the dielectric exclusion accounts for the interactions of ions with polarized interfaces between media of different dielectric constants. As a result of dielectric exclusion, both anions and cations are excluded from the membranes (nano)pores. In the case of charged NF membranes, Donnan exclusion was shown to be the main parameter determining the rejection.^{42, 52} In previous work, we showed that this was indeed true for membranes coated with (PDADMAC/PSS)₆-PDADMAC and (PDADMAC/PSS)₇.⁴² However, recent work of Bruening and co-workers showed that for charged LbL modified membranes, size exclusions can also be the main mechanism.⁵³ It was further shown that when Donnan effects and size exclusion do not suffice to describe the retention behavior, the dielectric exclusion needs to be taken into account.^{50, 51} To our knowledge, the effect of the presence of zwitterionic moieties in multilayers on the rejection mechanism for nanofiltration purposes has not been studied yet.

In Figure 6, the retention of CaCl₂, NaCl and Na₂SO₄ for the three different membranes is shown. No permeability changes were observed during the filtration of the electrolyte solution compared to the clean water permeabilities (3.9, 3.7 and 4.5 L·m⁻²·h⁻¹·bar⁻¹ for the membranes coated with 7(+), 8(z) and 9(-) layers respectively). The rejection results of the different salts by the membranes provide an insight of the major retention mechanism. The PSS terminated

Figure 6. Different ion retentions of the HFS membranes coated with (PDADMAC/PSBMA/PSS)₂/PDADMAC (+), (PDADMAC/PSBMA/PSS)₂/PDADMAC/PSBMA (z) and (PDADMAC/PSBMA/PSS)₃ (-). Ion feed concentration is 5 mM. The filtration is performed under cross-flow at turbulent conditions ($Re \gg 3,500$) and a trans-membrane pressure of 1.75 bar.

membrane indeed shows a typical Donnan behavior. Due to an increased Donnan exclusion of the bivalent sulfate anion by the negative membrane, almost complete retention (98%) for Na₂SO₄ is observed. The bivalent calcium cation on the other hand, is excluded the least by the negative membrane, resulting in only 20% retention for CaCl₂. In line with these results, the NaCl retention is found between that of Na₂SO₄ and CaCl₂. In contrast to the PSS-terminated membrane, neither the PDADMAC- nor the PSBMA-terminated membranes show clear Donnan behavior. For these membranes, which are positively charged, the retention of both Na₂SO₄ and CaCl₂ is higher compared to that of NaCl. If Donnan exclusion were prevalent, the expected order of salt retention would be CaCl₂ > NaCl > Na₂SO₄. This indicates that size and/or dielectric exclusion of Ca²⁺ and SO₄²⁻ dominate the retention. The difference between the salt retention of our differently terminated trilayers is remarkable and was not observed for PDADMAC/PSS bilayers. Therefore, any contributions from dielectric exclusion can only be attributed to the presence of the zwitterion PSBMA within the multilayer.

In addition to the retention behavior for different salts, the retention for a mixture of six micropollutants was also measured for membranes coated with 7 (+), 8 (z) or 9 (-) layers. The selected micropollutants are shown in Figure 3 and some important properties are listed in Table 1. During the selection, care was taken that positive, neutral and negative molecules were included. Furthermore, a wide range of hydrophilicity was taken. The octanol/water coefficients (log P) of the different micropollutants range from 0.49 (most hydrophilic) to 4.04 (most hydrophobic). The filtration experiments were conducted under similar circumstances as for the ion rejection measurements. As with the electrolyte solutions, no difference in permeability compared to the clean water permeability was observed during the measurement. Figure 7 shows the results, which have been color coded based on the micropollutant charge: green for positive micropollutants, black for neutral micropollutants and red for negative micropollutants.

For all three membranes, the micropollutant rejection mechanisms are comparable to those observed for the salt rejections. In the case of the PSS-terminated membrane, evidence of Donnan exclusion is found. Both naproxen and bezafibrate are negatively charged and show a high retention. This high retention is attributed to the charge repulsion of the negative membrane,

Figure 7. Retention of different micropollutants at pH 5.8 by HFS membranes coated with (PDADMAC/PSBMA/PSS)₂/PDADMAC (+), (PDADMAC/PSBMA/PSS)₂/PDADMAC/PSBMA (z), and (PDADMAC/PSBMA/PSS)₃ (-). Filtration experiments were performed under turbulent conditions ($Re \gg 3,500$) and at a trans-membrane pressure of 1.75 bar. Results are color coded based on the micropollutant charge: green for positive, black for neutral, and red for negative micropollutants.

and is comparable to the high SO_4^{2-} retention. A significantly lower retention is observed for the positively charged atenolol by the negative membrane, comparable to Ca^{2+} retention. Due to the opposite charges of the atenolol (positive) and the PSS-terminated membrane (negative) little charge repulsion exists, resulting in a lower retention compared to that of the negative micropollutants. The lack of charges of the three neutral micropollutants results in the lowest retention for these molecules, as no electric repulsion exists and the rejection is primarily based on size exclusion.

In contrast to the PSS-terminated layer, the PDADMAC- and PSBMA-terminated layers show high retention of all charged micropollutants. The three uncharged micropollutants have a significantly lower retention compared to that of the charged micropollutants. This is similar to that observed for the PSS terminated membrane, which also shows lower retention for uncharged species. Even though Donnan exclusion is not prevalent in the PDADMAC and PSBMA terminated membranes, the results from the micropollutant filtration show that the retention cannot be (solely) based on size exclusion. For these membranes no trend with respect of the molecular weight of the micropollutant is found, for example, for the PSBMA-terminated membrane, 70.4% of naproxen ($230.26 \text{ g}\cdot\text{mol}^{-1}$) is retained whereas only 7.2% of bisphenol A ($228.29 \text{ g}\cdot\text{mol}^{-1}$) is retained even though these molecules have similar dimensions.⁶ This means that, by the incorporation of the zwitterionic layer the dielectric exclusion determines the solute rejection. As a result, these membranes have a high retention for all charged solutes. This is a significant advantage in water treatment processes as more contaminants can be rejected in a single step as compared to membranes that only show Donnan exclusion.

6.4 Conclusion

Current challenges in our drinking water contamination require the development of much more sophisticated, specific, and straightforward purification techniques designed to remove low molecular weight contaminants based on direct nanofiltration (NF) with hollow fiber membranes. Such hollow fiber membranes should have a separation layer that rejects a multitude of contaminants. In this chapter, we present a new hollow fiber NF membrane based on PDADMAC (+), PSBMA (z) and PSS (-) trilayers coated from aqueous solutions onto a membrane support using the simple LbL coating approach. On model surfaces, the ionic strength of the coating solutions is found to be a key parameter to control the stability and growth of these layers, with the most stable layer growth obtained at 0.2 M NaCl. Under these conditions, the trilayers can also be successfully coated on charged porous membranes. The properties of the formed NF membranes depend strongly on the terminating layer. Due to the higher hydrophilicity of a PSS-terminated layer, membranes with a final PSS coating have a relatively higher water permeability compared to membranes that have a PDADMAC- or PSBMA-terminated layer. The retention of different solutes in water and the underlying mechanism change with the terminating layer. For all membranes the rejection of uncharged micropollutants is relatively low due to the lack of Donnan or dielectric exclusion. For PSS-terminated layers, clear evidence of Donnan exclusion is found, resulting in a membrane with Na_2SO_4 rejection of 98% at a permeability of $4.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. This Donnan exclusion is also manifested in the rejection of micropollutants, where only high rejection of negatively charged molecules is observed. For membranes with either PDADMAC- or PSBMA-terminated layers, the difference in the rejection of various ion pairs cannot be described by Donnan exclusion, and it is concluded that dielectric exclusion is the dominating rejection mechanism. As a result of this, membranes, terminated with either PDADMAC or PSBMA have a high retention for both positively and negatively charged micropollutants. This behavior is not seen for classical PDADMAC and PSS PEMs, and is therefore attributed to the incorporation of the polyzwitterion in the multilayer. Because these zwitterionic NF membranes are able to retain a wider variety of micropollutants, they are better suited for the removal of emerging contaminants from polluted water.

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Enhanced Stability of Zwitterionic Multilayer Membranes via Cross-Linking
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Zwitterionic Polyelectrolyte Multilayers For Stable Membranes

Abstract

This chapter encompasses the creation of a novel, highly stable membrane based on multilayers containing a zwitterionic copolymer. Zwitterionic multilayer membranes have great potential for antifouling membranes, but are inherently not stable at high ionic strength. We show that under various coating conditions, multilayers can be built with the zwitterionic copolymer poly(N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine-*co*-acrylic acid) (PSBMA-*co*-AA) and poly(diallyldimethylammonium chloride) (PDADMAC). When exposed to high ionic strengths, the layers readily decompose. However, cross-linking of the AA moieties within the multilayer leads to a unique and very stable zwitterionic multilayer membrane.

7.1 Introduction

The modification of polymeric membranes to enhance their performance has been widely applied. Out of the different modification techniques, the layer-by-layer (LbL) method has proven to be a viable and versatile method that does not require harsh coating conditions.¹ By alternately coating oppositely charged polyelectrolytes from aqueous solutions, a well-defined and controllable polyelectrolyte multilayer (PEM) can be applied onto a charged surface.² In addition to conventional polyelectrolytes, polymers with specific functionalities can be incorporated into the multilayer. As a result, this functionality can be transferred to the multilayer, for instance leading to stimuli responsive or low fouling multilayers.³⁻⁴ Especially the latter is of great interest in the field of membrane filtration, since fouling can lead to a loss of performance, an increase in process down-time, and to a reduction in membrane life-time due to necessary cleaning steps.⁵

A promising group of polymers for low fouling surfaces are zwitterionic polymers, bearing both positive and negative moieties on the same pendant group.⁶ Even though these polymers are inherently charge neutral, they have been used to build PEMs by utilizing the specific interactions between a strong polyzwitterion and a strong polycation.^{7,8} We showed that this approach can be used to create PEM membranes with nanofiltration properties,⁸ or even PEM membranes that are stimuli responsive.³ Alternatively, lowering the pH can render weak polyzwitterions temporarily charged allowing the growth of multilayers.⁹⁻¹⁰ These layers are readily removed at alkaline conditions and can potentially be used as sacrificial layers.⁹ A different approach to incorporate zwitterionic moieties into multilayers is by using a copolymer of a conventional polyelectrolyte and a polyzwitterion. Via this way, the PEM can be build based on the strong interactions between a polycation and a polyanion, while zwitterionic groups are still incorporated in the multilayer. This is a very promising route, one that has resulted in surfaces with pronounced lower non-specific adsorption of for instance muscle cells,¹¹ fibronectin,¹² and platelet and fibrogen.¹³ For the use of these zwitterionic PEMs in low fouling membrane filtration, a stable membrane performance under various conditions is a key factor in the future development of these membranes. This means that any changes in the layer, either responsive or destructive, are most unwanted. Regarding the stability of PEMs, the environmental ionic strength is always a major concern, since at high ionic strength the electrostatic interactions between the polyelectrolyte are screened which can lead to layer rearrangement or disintegration.¹⁴⁻¹⁵ The nature of the zwitterionic moieties, which results in an increased layer swelling at higher ionic strength, will further impair the layer stability.¹⁶

Therefore, this work specifically investigates the stability at increased ionic strength of a PEM on a membrane that consists of a zwitterionic copolymer and a polycation. For this a PEM membrane

Figure 1. Schematic representation of the multilayers made in this work based on PDADMAC and PSBMA-co-AA.

containing the zwitterionic copolymer poly(N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine-co-acrylic acid) (PSBMA-co-AA) is synthesized. This copolymer is known to have excellent anti-fouling properties.¹³ Multilayers are built under various conditions on both a silicon wafer and a polymeric membrane by alternately depositing the strong polycation poly(diallyldimethylammonium chloride) (PDADMAC) and zwitterionic copolymer PSBMA-co-AA. We show that these multilayers are readily formed, but do not have a good stability at increased ionic strengths. To improve the membrane integrity, the layers are subsequently cross-linked by a coupling reaction between the AA moieties and ethylenediamine to enhance the layer stability (see Figure 1), which indeed leads to the first example of zwitterionic PEM modified membranes with a stable performance.

7.2 Experimental

Materials

Acrylic acid (AA) and N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA) were obtained from Sigma Aldrich (The Netherlands). Poly(diallyldimethylammonium chloride) (PDADMAC, Mw = 150 kDa, 20 wt% in water) was obtained from Kemira (Finland). All other chemicals were purchased from Sigma Aldrich (The Netherlands). All chemicals were used without any further purification steps.

Copolymer Synthesis and Characterization

For the PSBMA-co-AA copolymer synthesis, 100 ml demineralized H₂O was flushed with nitrogen for 1 hour in a 500 mL round bottom flask. In this, 5.46 gram (19.5 mmol) SBMA was dissolved under a nitrogen atmosphere. The solution was heated to 50 °C, and 1.34 mL (19.5 mmol) AA was added. After 1 minute, 0.184 gram (0.8 mmol) (NH₄)₂S₂O₈ was added. The mixture was left to react under a nitrogen atmosphere for 7 hours. After the reaction, the mixture was cooled and poured into MeOH to form a precipitate. The precipitate was washed three times with 50 ml acetone and subsequently dried in a vacuum oven at 30 °C for 24 hours. The copolymer was stored under vacuum at 30 °C to prevent water uptake and was used without any other purification steps. The PSBMA-co-AA structure was verified with ¹H-NMR in D₂O with 0.2% M NaCl on a Bruker Ascend 400 MHz, according to the method of Kuo et al.¹³ The molecular weight was determined via MALLS with a 0.83 g·L⁻¹ copolymer solution in 0.2 M NaCl.

Multilayer Growth

The multilayer growth on silicon wafers was monitored by means of reflectometry.¹⁷ For this, 0.1 g·L⁻¹ PDADMAC and PSBMA-co-AA solutions with the appropriate ionic strength were prepared and alternatively adsorbed on a silicon wafer with a 75 nm SiO₂ top layer. A detailed description of the experimental procedure can be found elsewhere.³ In reflectometry, the ratio between the reflected p- and s-polarized light components, defined as S (-), is monitored and the change in this ratio (ΔS) is directly proportional to the amount of mass adsorbed on the wafer, according to equation 1:

$$\Gamma = \frac{\Delta S}{S_0} Q \quad (1)$$

where Γ is the amount of mass adsorbed on the wafer ($\text{mg}\cdot\text{m}^{-2}$), S_0 is the starting output signal of the bare silicon wafer (-), and Q is the sensitivity factor for the system ($\text{mg}\cdot\text{m}^{-2}$). To calculate the sensitivity factor, an optical model was used, based on the following values: $q = 71^\circ$, $n_{\text{silica}} = 1.46$, $\tilde{n}_{\text{silicon}} = (3.85, 0.02)$, $n_{\text{H}_2\text{O}} = 1.33$, $\text{dn}/\text{dc}_{\text{PDADMAC}} = 0.18 \text{ mL}\cdot\text{g}^{-1}$, $\text{dn}/\text{dc}_{\text{PSBMA-co-AA}} = 0.14 \text{ mL}\cdot\text{g}^{-1}$, $d_{\text{silica}} = 75 \text{ nm}$.^{3, 18} The sensitivity factor (Q) obtained to calculate the actual mass adsorption for all experiments was $30 \text{ mg}\cdot\text{m}^{-2}$.

Membrane Coating

The polymeric membranes used in this work were dense ultrafiltration membranes (Hollow Fiber Silica (HFS)), kindly provided by Pentair X-Flow (the Netherlands). These are capillary membranes with a sulfonated poly(ether sulfone) (SPES) separation layers. The membranes have an inner diameter of 0.8 mm and a molecular weight cutoff of 10 kDa.

For the membrane coating the same procedure described as in our previous work was used.³ Prior to coating the membranes with the polyelectrolytes, the fibers were wetted in a 15 wt% ethanol solution in water overnight and subsequently rinsed three times with demineralized water. The fibers were alternately dipped in a solution of $0.1 \text{ g}\cdot\text{L}^{-1}$ PDADMAC or PSBMA-co-AA with the appropriate ionic strength for 30 minutes. In between the different polyelectrolyte solutions, the fibers were washed in three solutions containing only background electrolyte at the same concentration for 10 min. in each solution. After each PSBMA-co-AA coating, membrane samples were taken for analysis. All membrane samples were put in a glycerol/water (15 / 85 wt%) mixture for 4 hours and dried overnight under ambient conditions.

For the crosslinking of the PEM modified layers, a N-hydroxysuccinimide (NHS) assisted carboxyl-amine conjugation with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and ethylenediamine was applied.¹⁹ For this, 10 freshly coated membranes were soaked in 250 ml of an aqueous solution containing 1.25 mmol NHS and 6.25 mmol EDC for 4 hours. After this, a $2.0 \text{ g}\cdot\text{L}^{-1}$ solution of ethylenediamine in water was slowly added, until a total of either 0.096, 0.039, or 0.013 mmol ethylenediamine. During all this, the pH was kept at 5.8 with 0.1 M HCl. The reaction was allowed to proceed for 24 hours at ambient temperature. Afterwards, the reacted membranes were immersed in a glycerol/water (15/85 wt%) mixture for 4 hours and dried overnight under ambient conditions.

Membrane Characterization

The dried membranes were potted in a module with a fiber length of approximately 150 mm with a polyurethane resin. The membrane permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) was determined by measuring the water flux through the membrane at 2.0 bar and normalizing the flux for the applied pressure. For the salt stability tests first the pure water permeability was measured, follow by the permeability of a 0.05 M NaCl solution. After this, again the pure water permeability was measured. These steps were repeated for 0.1, 0.2, 0.5, 1.0 and 1.5 M NaCl, again with a pure water permeability measurement in between each step. All filtration experiments were performed at room temperature. The membrane zeta-potential was measured as described in Chapter 6.

7.3 Results and Discussion

The PSBMA-*co*-AA copolymer synthesis successfully resulted in a water soluble polymer with a molecular weight of 600 kDa, as determined by MALLS in an aqueous solution with 0.2 M NaCl. ^1H -NMR was used to analyze the zwitterionic SBMA content (Figure 2), based on the method of Gui et al.¹³, which was found to be 67%. The higher SBMA content in the copolymer compared to that of the reaction mixture (50:50) is attributed to the higher reactivity of the methacrylate moieties compared to acrylic acid.²⁰

Figure 2. ^1H -NMR spectrum of the zwitterionic copolymer PSBMA-*co*-AA.

To understand the behavior of the zwitterionic multilayer buildup, reflectometry was used to monitor the growth of multilayers consisting of PSBMA-*co*-AA and PDADMAC on a silicon surface. The results from the reflectometry measurements (Figure 3a) give the mass adsorption on the silicon wafer per adsorbed layer and show that PDADMAC/PSBMA-*co*-AA multilayers can be built in an LBL fashion at various conditions. There is a notable dependence of the ionic strength and pH on the amount of mass adsorbed. At 0.005 M NaCl (pH 5.8) little material is deposited per coating step yielding approximately $10\text{ mg}\cdot\text{m}^{-2}$ after 8 bilayers. Increasing the ionic strength to 0.2 M NaCl (pH 5.8) increases the mass adsorption to $23\text{ mg}\cdot\text{m}^{-2}$ after 8 bilayers. This increase is comparable to the behavior of classical polyelectrolytes, that also show higher adsorption with increasing ionic strength due to an increase in extrinsic charge compensation.²¹ Remarkably, the layer mass after 8 bilayers is decreased when an even higher NaCl concentration of 0.5 M (pH 5.8) is used during coating, yielding only $4\text{ mg}\cdot\text{m}^{-2}$ after 8 bilayers. Additional experiments with layers grown from 0.5 M NaCl and at acidic conditions (pH 3), below the pK_a of AA, show an increase of the polymer adsorption from 4 to $6\text{ mg}\cdot\text{m}^{-2}$ after 8 bilayers. The dependence on the coating conditions of the PDADMAC/PSBMA-*co*-AA layers is similar to that observed for PDADMAC/PAA layers. Regarding the ionic strength, Dubas and Schlenoff found that for PDADMAC/PAA multilayers prepared at different salt concentrations, the film thickness has a maximum at around 0.3 M NaCl.¹⁵ For layers coated on a membrane, similar results were found by Ahmadiannamini et al., who also showed a thickness optimum for PDADMAC/PAA layers.²² Like the PDADMAC/PAA multilayers, our PDADMAC/PSBMA-*co*-AA also have an optimum layer thickness at an ionic strength around 0.2 M NaCl. With respect to the pH, Alonso

Figure 3. PDADMAC/PSBMA-co-AA multilayer buildup. A) Multilayer growth on a silicon wafer at different coating conditions. B) PEM modified membrane permeability after each additional bilayer, coated at different conditions. For all solutions the pH was 5.8, unless stated otherwise.

et al. reported that much thinner PDADMAC/PAA layers are formed at pH 3 compared to pH 6 or higher.²³ This is again similar to PDADMAC/PSBMA-co-AA multilayers, with an increase in layer mass at pH 3 compared to pH 5.8. The resemblance between the PDADMAC/PAA and PDADMAC/PSBMA-co-AA systems is a clear indication that the interactions of the polycation and the AA moieties within the copolymer govern layer buildup.

PDADMAC/PSBMA-co-AA multilayers were also coated on a polymeric hollow fiber membrane under comparable coating conditions. Membrane coating is monitored by means of changes in membrane permeability after each bilayer (Figure 3b) and the zeta-potential (Figure 4). For all coating conditions the membrane permeability drops with each additional coated bilayer. The zeta-potential measurements show a clear flipping of the membrane charge after each monolayer coating step due to charge overcompensation during polymer adsorption. The change in zeta-potential and the drop in membrane permeability after the different coating steps are a clear indication that a multilayer with zwitterionic copolymer can successfully be applied onto a polymeric membrane. With respect to the coating conditions and their effect on the membrane permeability, the same trends as with the reflectometry results are found. The steepest permeability decline is observed while coating at 0.2 M NaCl, indicating that the highest amount of polymer is adsorbed on the membrane per bilayer as also observed with the reflectometry experiments. At 0.5 M NaCl, the lowest permeability decline is observed which is also in agreement with the low adsorbed amounts as observed with reflectometry. Lowering the pH of the 0.5 M NaCl coating solution results in a significant higher drop in permeability, again as expected from our reflectometry results. The results clearly show that a membrane can successfully be coated with a multilayer based on the zwitterionic copolymer PSBMA-co-AA.

Coating on both the silicon wafer and the membrane indicates that the interactions in the multilayer are predominantly based on those between the AA moieties and the polycation. For PDADMAC/PAA multilayers it is known that these rapidly decompose at higher ionic strength.¹⁵ This can mean that also the PDADMAC/PSBMA-co-AA layers presented here have a low stability at high ionic strength. The stability of these multilayers deposited on a membrane was investigated by filtering solutions with different ionic strengths through the PDADMAC/PSBMA-co-AA modified membranes and monitoring the changes in the permeability. To assess

Figure 4. Membrane zeta-potential after each additional by-layer of PDADMAC and PSBMA-co-AA coated at 0.2 M NaCl (pH 5.8). Zeta-potential measurements are performed at pH 5.8 in 0.5 mM KCl.

if the observed changes are reversible, the pure water permeability was measured after each saline filtration step. Any differences between the pure water permeability before and after each saline filtration step are indicative of irreversible changes of the PEM.

The results in Figure 5 show that the PDADMAC/PSBMA-co-AA layer on the membrane is responsive to the ionic strength of the filtration solution. The membrane permeability increases when the ionic strength of the filtration solution increases, and then decreases again when filtering pure water. At 1.5 M NaCl, the permeability has increased by almost 100% compared to the pure water permeability. The relative increase in permeability seems independent on the coating conditions (Figure 5a). However, unlike the PDADMAC/PSBMA multilayers reported earlier,³ the responsiveness is not completely reversible. The pure water permeability of the membrane after filtration of the saline solution also increased by 60 to 100% after 1.5 M NaCl (Figure 5b). This increase in pure water permeability means that either a restructuring of the multilayer takes place that leads to a more open, permeable multilayer or that part of the multilayer is rinsed away

Figure 5. PEM modified membrane response to different electrolyte solutions. A) Relative permeability change in electrolyte solutions and pure water for membranes with (PDADMAC/PSBMA-co-AA)₅ layers coated at i) 0.005 M NaCl, pH 5.8 (black squares), ii) 0.2 M NaCl, pH 5.8 (blue triangles) and iii) 0.5 M NaCl, pH 3 (red circles). B) Membrane pure water permeability after exposure to different ionic strength.

during filtration at higher ionic strength. The latter is more likely, considering the magnitude of the permeability changes and the known instability of PDADMAC/PAA layers.¹⁵ The difference between the irreversible changes of PDADMAC/PSBMA-co-AA layers compared to the reversibility of the PDADMAC/PSBMA layers, must be attributed to the presence of the AA moieties. This supports the conclusion that the main interactions in the multilayers are indeed those between PDADMAC and AA. This lack of integrity of the modified membranes is a critical issue for a constant water filtration process and thus needs to be improved.

The stability of classical PEMs can be enhanced by covalent cross-linking of the multilayer after buildup.²⁴⁻²⁶ For zwitterionic polymers, our approach of using a copolymer allows for a cross-linking via the presence of the carboxylic acid group. This was done via a N-hydroxysuccinimide (NHS) assisted carboxyl-amine conjugation with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and ethylenediamine.¹⁹ For the cross-linking, the membranes are soaked in a solution of 5 mM NHS and 25 mM EDC. After 4h, ethylenediamine was gradually added to the solution and the cross-linking reaction was allowed to proceed for 24 h. The zeta-potential of the membrane before and after cross-linking is measured in order to monitor a successful reaction of the ethylenediamine with the AA moieties (Figure 6). After the reaction, the membrane zeta-potential has noticeably shifted to a more positive membrane with a higher iso-electric point. This increase is attributed to a loss of the negative AA groups via the conjugation with ethylenediamine. While the zeta-potential measurements indicate a successful reaction of the ethylenediamine, this does not directly constitute to crosslinking of the multilayer. The reaction can also have resulted in a mere grafting of ethylenediamine on the AA groups, for instance due to an excess of ethylenediamine or a lack of chain mobility. Therefore, successful crosslinking is assessed by exposing the reacted membrane to different electrolyte solutions and measuring any changes in permeability. The results for the membranes coated at 0.005 M NaCl after reaction with three different EDC concentration is shown in Figure 7. First of all, the results show that in all cases the membrane permeability drops after the reaction to

Figure 6. Membrane zeta-potential before and after cross-linking with 0.096 mmol EDC. Measurement performed in 5 mM KCl.

Figure 7. Permeability change of (PDADMAC/PSBMA-co-AA)₈ (0.005 M NaCl) coated membrane before cross-linking (●) and (PDADMAC/PSBMA-co-AA)₈ (0.005 M NaCl) coated membranes after cross-linking with 0.096 mmol (×), 0.039 mmol (⊗) and 0.013 mmol (*) EDC.

Figure 8. Permeability change of $(\text{PDADMAC/PSBMA-co-AA})_8$ coated membrane before cross-linking and after cross-linking with 0.096 mmol. Black symbols for membranes coated at 0.2 M NaCl (pH 5.8) and blue symbols for membranes coated at 0.5 M NaCl (pH 3).

approximately $14\text{--}18\text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, an indication that the PEM has become more dense due to cross-linking. Secondly, upon increasing the salt concentration, the permeability of the reacted membrane remains constant. This is both the case for the permeability of the saline solutions as for the pure water permeability. Similar results are found for reacted membranes coated at 0.2 M NaCl (pH 5.8) and 0.5 M NaCl (pH 3.0), see Figure 8. The drop in permeability, and more importantly the lack of ionic strength responsiveness after the reaction with ethylenediamine are clear indications that successful cross-linking of the multilayer took place. By covalently binding of the PSBMA-co-AA polymers in the multilayers, a cross-linked network has been formed that does not swell or (partly) dissolve when exposed to higher ionic strengths. This means that the obtained membranes can be used in a variety of applications, including those that contain feed solutions with high ionic strengths.

7.4 Conclusions

In this work we demonstrate that the zwitterionic copolymer PSBMA-co-AA can be successfully used in the layer-by-layer modification of a hollow fiber membrane. This copolymer has a high potential with respect to reduced fouling properties of the modified surface. We show that the main interactions that govern the layer buildup are between the AA moieties of the copolymer and the polycation PDADMAC. However, the PEM on the membrane has a relatively low stability at increased ionic strength. Already at 0.05 M NaCl, loss of the multilayer is observed. At 1.5 M NaCl multilayer decomposition leads to an irreversible increase of the membrane permeability of 60–100%. This will impair the membrane integrity under operating conditions. The stability of the zwitterionic PEM on the membrane is successfully enhanced by cross-linking the PEM. As a result, for the first time a membrane functionalized with a multilayer bearing zwitterionic groups that is stable to a NaCl concentration of up to 1.5 M NaCl is reported. This enhanced stability of the zwitterionic PEM presented here is essential for the application of these multilayers in membrane technology where a variety of process conditions will be encountered.

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*"It was the best of times, it was the worst of times,
it was the age of wisdom, it was the age of foolishness,
it was the epoch of belief, it was the epoch of incredulity,
it was the season of Light, it was the season of Darkness,
it was the spring of hope, it was the winter of despair,
we had everything before us, we had nothing before us,
we were all going direct to Heaven, we were all going direct the other way."*

Charles Dickens

A Tale Of Two Cities, 1859

Epilogue

A Tale Of Two Charges, Indeed

Throughout this thesis, the interactions of positive and negative charges, be it from a substrate, a dissolved polyelectrolyte, a polyzwitterion, micropollutants or free mobile ions, are investigated and discussed. This certainly justifies the title of the thesis. These different interactions between charged moieties allow for controlling, or tuning, the properties and thus the performance of polyelectrolyte multilayer modified membranes. First we showed that a proper selection of the substrate charge and the type of polycation can lead to a long lifetime of the membrane. Then we showed that the amount of free mobile ions and the charge of the final polyelectrolyte can change the permeability and selectivity of the membrane. This is the case for membranes coated with classical polyelectrolytes, but also when a zwitterionic polymer is incorporated. These results clearly highlight the potential of PEM modified membranes.

So, what is next?

In this chapter, challenges and foreseen future developments of PEM modified membranes for water treatment processes are discussed. Several aspects that are important for a successful valorization will be covered and finally, the main incentive of the thesis will be revisited.

8.1 Membrane Selectivity

The most important property of a membrane is its ability separate different components from each other. In order to do this efficiently, a high selectivity between the two components is key. For water treatment membranes this comes down to a high transport of water and a low passage of ions, micropollutants or other contaminants. As such, there is a trade-off between a layer that has a water permeability high enough to make the process economically viable, but dense enough for an adequate rejection of the solutes. With respect to this, the layer-by-layer technology has a huge potential. Compared to other methods to obtain a dense layer on a membrane, the PEM can be made extremely thin. It can even be up to an order of magnitude thinner than the well-known thin film composite (TFC) polyamide layers that are now widely used in commercial nanofiltration (NF) and reverse osmosis (RO) membranes. As the resistance of the water transport through a dense film is directly proportional to the thickness of that layer, PEM have the potential to lead to membranes with permeabilities that are an order of magnitude higher than that of the TFC membranes. Of course, this will only be viable if the rejection of contaminants or ions is maintained. Until now, we are not aware of any PEM modified membranes that indeed fulfill the criteria of both thin and dense films such that they can directly compete with the TFC RO (or even NF) membranes. One wonders why.

A reason for this can be that the PEMs are intrinsically not dense enough to have the necessary selectivity. The chemical structure of the PEM is different compared to that of TFC membranes: where the TFC membranes are covalently cross-linked via an amide bond, the PEM layers are ionically cross-linked. This can result in an (intrinsic) difference of the pore size of the two types of layers. The pore radius of a PEM was estimated to be 0.41 nm for PDADMAC/PSS layers and 0.34 to 0.5 nm for PAH/PSS layers.¹ These values are very comparable to the estimated pore size of some commercial membranes, which are estimated to be 0.2 to 0.8 nm for TFC RO and 0.4 to 1.2 nm NF membranes.²⁻⁴ It must be noted that for the PEM membranes the density of the multilayer is, next to the type of polyelectrolytes, very much dependent on the ionic strength applied during coating.⁵ We showed this in Chapter 3 of this thesis, where higher NaCl retentions are obtained for membranes coated with PDADMAC/PSS at 0.05 M NaCl as compared to 0.5 M NaCl. This also seems to be reflected in the estimated pore size of the multilayer (although a detailed investigation is lacking): a PAH/PSS layer grown at pH 1.7 without any further ionic strength adjustment resulted in a PEM with a pore radius of 0.34 nm,¹ whereas PAH/PSS layers coated at pH 2.1 in 0.5 M showed a pore radius of 0.52 nm.⁶ This is also highlighted by the results presented in Figure 1 (work in collaboration with Pentair X-Flow), which shows a comparison of PEM and TFC membranes. Depending on the type of PEM, comparable NaCl retentions can be obtained but with a significantly higher membrane permeability. The next step should be is a further enhancement of the selectivity up to +99% NaCl rejection. These results suggest that similar densities can be obtained as with TFC membranes, if the correct coating conditions and polyelectrolytes are applied.

Another reason that the PEM modified membranes do not (yet) outperform the current TFC membranes could be that defects in the ultrathin multilayer impair the bulk membrane selectivity. Coating of a 5 mg·m⁻² film on a hollow fiber is analogous to covering an average sized rugby pitch with 2 table spoons of sugar. It seems not unlikely that small pinholes will occur. Such defects were indeed observed by Cheng et al., who reported a drop in K⁺/Mg²⁺ selectivity of more than an order of magnitude when switching from diffusive to convective transport.⁷ Such

Figure 1. Comparison of different PEM and TFC membranes. NaCl rejection is measured at 4 bar under turbulent crossflow conditions. Courtesy of Pentair X-Flow.

defects can be reduced or avoided by coating more layers, up to 30 to 60 or more.⁸ However, even if the practical implications (or limitations) of this remedy are accounted for, the high number of coatings will lead to a relatively thick separation layer. This means that a main benefit of the PEM, making ultrathin layers, is annulled. Preferably another solution to prevent any defects should be pursued.

For a defect free ultrathin layer, the support on which the PEM is coated needs to be uniform and accessible to the polyelectrolytes at a nanoscale. Throughout this work we tried to achieve this by wetting the membrane for a long time prior to coating. Our initial results (not reported) showed that this lead to a better reproducibility of the coating. It is reasoned that un-wetted surfaces are less covered by the polyelectrolytes during coating, leading to less reproducible results. We are however unaware if our wetting does indeed results in a complete coverage of the membrane and this is something that should be investigated in more detail. Initial results from Menne et al. showed that an active transport of the polyelectrolyte to the membrane surface also significantly enhances the properties of the coated membrane.⁹ These results are an indication that indeed good coverage of the ultrathin layer is key in the development of PEM modified membranes.

If, for any reason, a complete coverage cannot be ensured on full scale, the problem of small defects can also be solved by utilizing again the versatility of the LbL method. If the membrane is first coated with a relatively thick but open layer (e.g., by coating at a high ionic strength), the

Figure 2. Small pinholes in ultrathin layers (A) could be avoided by coating a thicker PEM with a higher resistance (B) or by coating asymmetric layers where the main resistance is in the ultrathin top layer (C).

resistance of this layer will be relatively low but complete coverage could be ensured. Obviously this membrane will have a low selectivity. However, when on top of that open layer a thin yet very dense layer is coated, the selectivity of the membrane can be enhanced while keeping an overall low resistance (Figure 2). In Chapter 5 we already showed that different multilayers can be built on top of each other, but we do not know to what extent the different layers mix. For an ideal asymmetric PEM structure as depicted in Figure 2, the interdiffusion of the two different multilayer systems should be limited. This is something that can be controlled by the type of polyelectrolyte and the coating conditions,¹⁰ but will require a detailed investigation both on the intrinsic properties of the layers as well as on the membrane performance.

8.2 Operating Costs

At the start of this thesis a clear statement is made that a next step in cheaper water treatment technology is the decentralization of water treatment facilities. Besides smaller plants, this will also require a much simpler processes. That is why we opted for the hollow fiber geometry, which allows for skipping an extensive pretreatment step. The direct filtration of surface water with a hollow fiber nanofiltration membrane has indeed shown to result in a stable membrane performance (see Figure 3).¹¹ The membrane used in that study is a relatively open nanofiltration membrane with a molecular weight cutoff of 1,000 Da, designed to reduce the total organic content of the water. The direct filtration with the hollow fiber was able to successfully substitute three conventional process steps, namely coagulation and flocculation, sedimentation and rapid sand filtration. As an added bonus, the hollow fiber based process even outperformed the conventional process with respect to the total organic content removal. The lack of spacers in the hollow fiber prevented clogging and thus a relatively low fouling rate of the membrane was observed. This means that membrane cleaning-in-place was only needed on a weekly to monthly basis. This example underlines the advantages of the hollow fiber geometry, something that is currently also further investigated in two European FP7 projects LbLBRANE and CERAWATER, and justifies the choice for this geometry for decentralized facilities.

Figure 3. Operational flux and membrane resistance of a hollow fiber NF membrane used for the direct filtration of surface water. Courtesy of Pentair X-Flow.

Besides the membrane geometry, the surface chemistry of the membrane also contributes to a reduction of the operational costs. First of all, the life time of the separation layer, and thus the membrane, is important. When the membrane will age rapidly, it will result in high replacement

costs. In the Chapter 2, we showed that adequate life times for PEM modified membranes can indeed be expected if the correct polyelectrolytes are chosen. Using the quaternary polycation PDADMAC in the multilayer results in an estimated membrane life time that is comparable to that of commercial ultrafiltration membranes (see Chapter 2 of this thesis). However, at this point a difficult trade-off is encountered. While quaternary polycations show a higher membrane life time, which will reduce their costs, they also have a lower charge density. The latter will result in a lower membrane selectivity.^{1, 8} On the other hand, polycations with a high charge density (e.g., PAH) are primary polycations that are readily degraded by hypochlorite. So, either one makes membranes that can be cleaned often with a lower selectivity, or one makes very selective membranes that need to be replaced more often.

Polyzwitterions may provide a solution for this trade-off. Polyzwitterionic membranes can reduce the amount of chemical cleanings, as polyzwitterions are, next to the “anti-polyelectrolyte effect” studied in this thesis, also well-known for their anti-fouling behavior. Although the exact mechanism behind the anti-fouling behavior of polyzwitterions is not quite understood, different theories point to a reduction of the entropy term of the non-specific adsorption.¹²⁻¹⁴ In membrane technology, most anti-fouling strategies are in fact based on reducing the enthalpy term of non-specific adsorption by rendering the membrane surface more hydrophilic.¹⁵⁻¹⁸ Surprisingly, entropic contributions are almost never considered in these membrane fouling studies. Nevertheless, zwitterionic modified membranes have investigated with respect their reduced fouling properties.¹⁹⁻²³ Initial results from the zwitterionic multilayers used in this thesis show indeed a reduced bovine serum albumin (BSA) adsorption on both silicon wafers as on membranes (Figure 4). A comparison is made between PDADMAC-, PSBMA-, and PSBMA-co-AA-terminated layers. Both PSBMA- and PSBMA-co-AA-terminated layers do not show any BSA adsorption, demonstrating their anti-fouling behavior. The PSBMA-terminated layer even

Figure 4. Fouling behavior of different surfaces. Left: adsorption from a 0.1 g·L⁻¹ BSA solution, measured with reflectometry on different polyelectrolyte layers. From top to bottom: PDADMAC, PDADMAC/PSBMA, PDADMAC/PSBMA-co-AA. Right: Fouling during filtration of 1.0 g·L⁻¹ BSA solutions of three different modified membranes. From top to bottom: HFS-PDADMAC_{0.2 M NaCl}, HFS-PDADMAC/PSBMA_{0.2 M NaCl}, HFS-PDADMAC/PSBMA-co-AA_{0.2 M NaCl}. For all experiments presented, the NaCl concentration was 0.2 M NaCl and the pH was 5.8.

shows some desorption of material on the wafer during exposure to BSA. Most probably, soluble complexes of BSA and PSBMA are formed that result in partial loss of the layer. Analogue to this, initially the membrane permeability slightly increases during the filtration of the BSA solution. For the PSBMA-*co*-AA-terminated layers, no BSA adsorption on the wafer and only a small permeability decline of the membrane are observed. On the other hand, for the PDADMAC-terminated membrane, we did observe a significant permeability decline during the filtration of a BSA solution. Also clear BSA adsorption on the PDADMAC-terminated layer on the silicon wafer was found. The reduced fouling behavior of the zwitterionic multilayers can be used to lower the need for chemical cleanings in a full scale plant, in that way enhancing the membrane lifetime and reducing its costs. This is especially useful if the more stable quaternary polycation cannot be used, as they can lead to membranes with a lower selectivity.

8.3 Conclusion

It so seems that several chapters can be added to the “Tale of Two Charges”, by continuing the study of all the different interactions between charges for PEM modified membranes. The reader very familiar with the actual source of the title of this thesis might already have identified an additional reasoning for the choice of the title. To me, Charles Dickens’ book on the French Revolution “A Tale of Two Cities” is about making the right decisions under challenging circumstances. The characters in the book are often confronted with making difficult decisions and the reader is made clear that most things turn out not to be so straightforward.^a Herein lies a great resemblance with the current situation in global accessibility to safe water, where we are also facing some major questions.

From a broad technological point of view, we can choose between different methods to treat the water: established large scale systems, or new, small scale systems? Will a single barrier suffice or do we need multiple barriers to ensure safe drinking water? For dense filtration membranes, a careful assessment has to be made between the trade-off of membrane selectivity and operational costs. I am sure that in time, scientists will come with answers and solutions to these problems.

However, also from a more sociological point of view, important decisions need to be addressed. Should our water be just safe enough, allowing for limited amounts of contaminants, or should we want an absolute removal of any harmful contaminants? What are acceptable costs to make our drinking water safe? Are there more important issues that have priority over safe drinking water? As a scientist, only the possible options for such questions can and will be given, unfortunately not a complete answer. These will have to come from a joint effort of dedicated scientific, industrial and governmental partners.

Personally, I hope they will go for the purest and safest option.

^a For example, Mr. Lorry tells Mr. Darna:

If you knew what a conflict goes on in the business mind, when the business mind is divided between good-natured impulse and business appearances, you would be amused, Mr. Darna.

The reader is also often shown that there is another side of the coin. On the one hand, Dickens clearly states the wrong doings of the French Revolution, for instance in the following passage, where he states the new judgmental system of the Republic synonymous with the guillotine:

“How goes the Republic?”

“You mean the Guillotine. Not ill. Sixty-three to-day. We shall mount to a hundred soon.”

On the other hand, he later also criticizes the established justice of the English aristocrats:

Death is Nature’s remedy for all things, and why not Legislation’s?

Accordingly, the forger was put to Death; the utterer of a bad note was put to Death; the unlawful opener of a letter was put to Death; the purloiner of forty shillings and sixpence was put to Death; the holder of a horse at Tellson’s door, who made off with it, was put to Death.

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Summary

Accessibility to safe drinking water is and will always be essential to human life. When not readily available, several techniques already exist to increase the water quality to a more potable standard at an acceptable price. Depending on the type of water to be treated, these techniques are designed to remove harmful bacteria and viruses or to desalinate brackish or seawater. However, with the increase in our population and the subsequent intensification of our water (re)use, different contaminants are appearing. These are small, unwanted, organic molecules, e.g., hormones, medicines, pesticides, some of which can, even at low concentrations, disrupt the endocrine system. Because current (waste) water treatment methods are not specifically designed for these emerging contaminants, the need for a treatment method capable of the removal of these low molecular weight contaminants is foreseen. Besides, most water treatment plants currently are large, centralized facilities that require substantial capital and personal investments, resulting in additional geographical and economic barriers. This means that nowadays in developing countries there are plenty of people still deprived of fresh drinking water. Decentralizing the water treatment based on a low cost and simple process, keeping the emerging contaminants in mind, is the next step in increasing the accessibility of potable water all over the world.

In this thesis, the development of selective membranes for water treatment facilities to cope with the aforementioned issues is covered. By using hollow fiber membranes, the water purification process can be simplified compared to using spiral wound membranes, a significant advantage for decentralized water treatment plants. The selectivity of ultrafiltration membranes is improved by coating a dense separation layer on the membrane. For this, the simple and versatile “layer-by-layer” (LbL) technique is used. By exposing a negative substrate to a polycation in an aqueous solution, a thin layer of that polycation is adsorbed on the surface. With the modified substrate, now positively charged, the same process can be done with an aqueous solution of a polyanion. This process can be repeated over and over again, steadily building a polyelectrolyte multilayer on top of the substrate. If the chosen substrate is a porous support (e.g., an ultrafiltration membrane), the formed polyelectrolyte multilayers can be used as a selective layer in water purification. The versatility of the LbL technique allows for an easy control over layer properties, such as thickness, density and charge, by varying the coating conditions, the type of polyelectrolytes and the amount of layers. This versatility makes the LbL system well suited for the design of dense filtration layers.

A key property of all membranes for water treatment purposes is the life time of the membrane. In this thesis we show that an adequate membrane life time can indeed be obtained for polyelectrolyte multilayers modified membranes, if certain criteria are met (**Chapter 2**). First of all, the presence of ionic groups on the membrane support significantly enhances the adherence of the multilayer on the membrane when high shear forces and reversed flow are applied. Second, the capability to withstand chemical degradation by hypochlorite is superior when quaternary ammonium polycations are used in the layer. We show that when both criteria are met, backwashable hollow fiber nanofiltration membranes can be made with a life time that is comparable to commercial ultrafiltration membranes.

Since the obtained multilayers can be as thin as a couple of nanometers, typical membrane characterization techniques (e.g., scanning electron microscopy) are not sensitive enough to visualize the layer on the membrane. Therefore, throughout this thesis, the buildup of multilayers is initially monitored via reflectometry on a model surface and subsequently correlated to changes in membrane performance when similar layers are adsorbed onto the fiber. Furthermore, by carefully assessing the differences in the membrane performance between a polycation or a polyanion terminated layer (the so-called odd-even effect), we identified that the multilayer can either be coated inside or on top of the pores of an ultrafiltration membrane (**Chapter 3**). When coating porous membranes with a relative large pore size, a transition is observed from coating in the pores to coating on top of the pores. By opting for a membrane with smaller pores, coating only on top of the pores is ensured.

The strength of the LbL technique is that a variety of polyelectrolytes and coating conditions can be used, all contributing the final properties of the ultrathin multilayer. Increasing the ionic strength results in thicker layers per coating step, both on model surfaces and on the hollow fiber membranes. On the membrane this leads to an increased in resistance per coating step, due to enhanced coverage of the membrane pores (**Chapter 3**). However, these thicker layers are also more open, resulting in a loss of ion/water selectivity. This means that when designing PEM modified membranes, it is essential that both the amount of layers and the ionic strength during coating are regarded in optimizing and controlling the PEM modified membrane properties.

Next to the classical polycations and polyanions, polyzwitterions for membrane filtration purposes have also been investigated for this thesis. Polyzwitterions are charged polymers that have both a positive and a negative charge on the same pendant group. The most notable properties of the polymers are their tendency to reduce fouling and their response to electrolyte solutions. Unlike polyelectrolytes, the solubility of polyzwitterions is increased at higher salt concentration, the so-called “anti-polyelectrolyte effect”. For a water insoluble zwitterionic copolymer it is shown that thin polymer film swelling in an aqueous solution significantly increases with the amount of zwitterionic groups and that the extent of the swelling is a function of the salt concentration and type of electrolyte (**Chapter 4**).

A water soluble polymer containing only zwitterionic pendant groups is successfully incorporated into a multilayer with a polycation. In the layer buildup, the anti-polyelectrolyte effect is manifested by the response to the ionic strength during the coating solutions. In contrast to classical polycation/polyanion multilayers, for the polycation/polyzwitterion layers the layer thickness is decreased when coating at higher ionic strengths. The permeability of the obtained membranes is shown to be responsive to the ionic strength during filtration, with an increase in permeability of >100% when switching from pure water to a 1.5 M NaCl filtration solution (**Chapter 5**). Again, this is attributed to the anti-polyelectrolyte effect. In cases that this responsiveness is not wanted, we show that crosslinking a zwitterionic multilayer negates this effect (**Chapter 7**). The crosslinking yields membranes that have a stable, non-responsive, permeability when filtering solutions with an ionic strength of up to 1.5 M NaCl. The polyzwitterion is also incorporated into a multilayer bearing both a polycation and a polyanion. The presence of the polyzwitterion changes the selectivity of the coated membrane, for both inorganic electrolytes and low molecular weight organic micropollutants. Incorporating the polyzwitterion PSBMA into the films leads to PEM membranes that are suited for removal of both positive and negative charged solutes (**Chapter 6**).

This work highlights the possibilities of PEM modified membranes for water purification, by being able to tune the final membrane properties not only by changing the coating conditions but also by selecting different charged polymers. With a good understanding of the nature and buildup of the multilayer, the combination of the LbL technique with hollow fiber membranes can be the next step in ensuring safe drinking water throughout the globe.

Samenvatting

Toegang tot schoon drinkwater zal altijd essentieel zijn voor ons leven. Wanneer het niet voorradig is kunnen er verschillende technieken gebruikt worden om de kwaliteit van het water tegen een acceptabele prijs te waarborgen. Afhankelijk van het te behandelen water zijn deze technieken uitermate geschikt om virussen, bacteriën of zouten uit het water te verwijderen. Maar met de groei van het aantal mensen, en het daarmee gepaarde intensievere (her)gebruik van ons water, komen er nieuwe verontreinigingen in ons water. Dit zijn kleine, ongewenste, moleculen zoals hormonen, medicijnresten en pesticiden. Deze stoffen kunnen, zelfs bij zeer geringe concentraties, schadelijk zijn voor dier en mens. De huidige (afval)water behandelingsmethodes zijn niet specifiek ontwikkeld voor deze opkomende microverontreinigingen. Vandaar dat de noodzaak van een nieuwe water zuiveringsmethode wordt verwacht, één die daadwerkelijk gericht is op de opkomende microverontreinigingen. Naast dit probleem van de microverontreinigingen, is er ook een probleem met de schaal van de meeste water zuiveringsinstallaties. Over het algemeen zijn dit grote, gecentraliseerde installaties die flinke investeringen vragen, zowel in kapitaal als in opleiding. Dit zorgt voor economische en geografische barrières in de voorziening van schoon drinkwater. Als gevolg hiervan zijn er, vooral in ontwikkelingslanden, nog steeds mensen die geen fatsoenlijke toegang hebben tot veilig water. Het decentraliseren van waterzuiveringsinstallaties op basis van een goedkoop en simpel proces samen met een focus op de verwijdering van de opkomende microverontreinigingen, is een volgende stap in de beschikbaarheid van schoon drinkwater over de hele wereld.

In deze dissertatie is de ontwikkeling van selectieve membranen beschreven die vooral gericht zijn op de bovengenoemde uitdagingen. De membranen zijn holle vezels, een geometrie die een eenvoudig proces zonder voorbehandeling mogelijk maakt. Dit is een groot voordeel voor gedecentraliseerde waterzuiveringsinstallaties. De selectiviteit van de membranen wordt verhoogd door een dichte laag te coaten op de membranen. Dit is gedaan via de “laag-bij-laag” (LbL) methode. Door een negatief geladen substraat bloot te stellen aan een positief geladen polyelektrolyt, adsorbeert een dunne laag van dit polyelektrolyt aan het substraat. Met het gemodificeerde substraat, nu positief geladen, kan hetzelfde worden gedaan met een negatief geladen polyelektrolyt. Dit gehele proces kan onbeperkt herhaald worden, zodat er langzaam een multilaag van polyelektrolyten op het substraat groeit. Wanneer het gekozen substraat een poreus membraan is, wordt er zo een dichte polyelektrolyt laag op het membraan gevormd die kan dienen als selectieve laag voor in de waterzuivering. De veelzijdigheid van de LbL techniek zorgt ervoor dat de eigenschappen van de selectieve laag nauw kunnen worden gecontroleerd. Dit maakt de LbL techniek uitermate geschikt voor het ontwikkelen van selectieve membranen.

Een belangrijk aspect van membranen die gebruikt worden in de waterbehandeling is de levensduur van de membranen. In dit werk laten wij zien dat wanneer aan bepaalde criteria wordt voldaan, er daadwerkelijk een adequate levensduur behaald kan worden met LbL gemodificeerde membranen (**Hoofdstuk 2**). De aanwezigheid van ionisch geladen groepen aan het te coaten membraan zorgt voor een veel betere hechting van de multilaag aan het membraan. Daarnaast bepaalt de keuze van het polykation de stabiliteit van de multilaag in een chloorbleekloog oplossing. Wij laten zien dat de levensduur van de LbL gemodificeerde membranen vergelijkbaar kan zijn aan commercieel succesvolle ultrafiltratie membranen.

Om een goed begrip te krijgen van de gevormde lagen op het membraan, wordt gedurende dit onderzoek de groei van de multilaag ook gevolgd op modeloppervlaktes. Dit is gedaan met behulp van reflectometrie. De groei van de multilagen op modeloppervlaktes wordt vervolgens gecorreleerd aan de verandering van de membraanprestaties. Door tevens te kijken naar het verschil tussen membranen welke zijn getermineerd met een polykation of met een polyanion (het even-oneven effect), is aangetoond dat een poreus membraan zowel gecoat kan worden in de poriën, als op de poriën (**Hoofdstuk 3**). Bij coating van een membraan met relatief grote poriën, is een overgang geobserveerd van coaten in de poriën naar coaten op de poriën. Wanneer er een membraan wordt gekozen met veel kleinere poriën, wordt er direct op de poriën gecoat.

De kracht van de LbL methode is dat de coatingcondities de eigenschappen van de laag bepalen. Coaten bij een hogere ionsterkte zorgt voor een dikkere multilaag. Op het membraan zorgt dit voor een grotere verhoging van de weerstand van het membraan per coating stap. Daartegenover staat dat de dikkere lagen ook minder dicht gepakt zijn. Op het membraan resulteert dit in een verlies van ion/water selectiviteit wanneer de multilaag bij een hogere ionsterkte is gecoat (**Hoofdstuk 3**).

Naast klassieke polykationen en polyanionen zijn er in dit onderzoek ook polyzwitterionen onderzocht. Polyzwitterionen zijn polymeren die zowel een positieve als een negatieve groep aan hetzelfde monomeer hebben zitten. Specifieke eigenschappen van deze polyzwitterionen zijn een lage niet-specifieke adsorptie en een karakteristieke respons in elektrolyt oplossingen. Terwijl polykationen en polyanionen slechter oplossen bij verhoogde ionsterkte (uitzouten), is

de oplosbaarheid bij polyzwitterionen beter bij verhoogde ionsterkte. Dit wordt wel het “anti-polyelektrolyt effect” genoemd. Voor een zwitterionisch copolymeer dat niet in water oplosbaar is, zorgt dit voor een verhoogde zwelling van het polymeer bij een hogere ionsterkte. Tevens is de zwellingsgraad afhankelijk van het type ionen (**Hoofdstuk 4**).

Water oplosbare polyzwitterionen zijn succesvol gebruikt in combinatie met een polykation om zwitterionische multilagen te maken. Ook in de opbouw van de zwitterionische multilagen manifesteert het anti-polyelektrolyt effect zichzelf. In tegenstelling tot klassieke multilagen worden dunnere zwitterionische multilagen gevormd bij hogere ionsterkte (**Hoofdstuk 5**). Daarnaast is de permeabiliteit van membranen gecoat met de zwitterionische multilaag responsief aan de ionsterkte van het te filteren water. Het verhogen van de zout concentratie van 0 tot 1.5 M NaCl zorgt voor een reversibele verhoging van de permeabiliteit van meer dan 100% (**Hoofdstuk 5**). Wanneer dit responsief gedrag niet gewenst is, kan dit worden tegengegaan door het covalent crosslinken van de multilaag. De membranen met een gecrosslinkte multilaag hebben een stabiele permeabiliteit tot en met 1.5 M NaCl (**Hoofdstuk 7**). Membranen zijn ook gecoat met multilagen bestaande uit een polykation, een polyzwitterion en een polyanion, wat resulteert in een nanofiltratie membraan met unieke eigenschappen. De aanwezigheid van het polyzwitterion verandert de selectiviteit van het nanofiltratie membraan zodat het zowel positief als negatief geladen opgeloste stoffen tegenhoudt. Dit gedrag is gezien voor zowel multivalente ionen als voor microverontreinigingen (**Hoofdstuk 6**).

Dit werk onderstreept de mogelijkheden van polyelektrolyt multilaag gemodificeerde membranen in nieuwe waterzuiveringsmethodes. De eigenschappen van de gemodificeerde membranen kunnen gestuurd worden door de selectie van polymeren en door de coating condities. Met een goed begrip van de groei en de karakteristiek van de multilaag, kan de LbL techniek de volgende stap zijn in een wereld vol schoon drinkwater.